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THE UNIVERSITY OF ALBERTA

FREE-RADICAL REARRANGEMENT IN A BICYCLIC SYSTEM

by

ALAN GIFFARD RYAN

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE

OF

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THE UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled

"FREE-RADICAL REARRANGEMENT IN A BICYCLIC SYSTEM"

submitted by ALAN GIFFARD RYAN in partial fulfilment of the requirements for the degree of Master of Science.

TO

MY MOTHER

MY WIFE

MY DAUGHTER

What is better than wisdom? Woman.

And what is better than a good woman? Nothing.

Chaucer

A B S T R A C T

The dibenzobicyclo[2.2.2.]octadien-7-yl free radical and the dibenzobicyclo[3.2.1.]octadien-2-yl free radical were investigated with the intention of gaining insight into the possibility of interconversion of the radicals by means of a 1,2-phenyl migration (neophyl rearrangement). The desired radicals were generated by the peroxide-initiated decarbonylations of 7-formyldibenzobicyclo[2.2.2.]octadiene and a mixture of exo- and endo-2-formyldibenzobicyclo[3.2.1.]octadiene.

Rearrangement is found only in the decarbonylation of 7-formyldibenzobicyclo[2.2.2.]octadiene; in this reaction is produced dibenzobicyclo[3.2.1.]octadiene, dibenzobicyclo[2.2.2.]octadiene and coupling products derived from the dibenzobicyclo[3.2.1.]octadien-2-yl radical and initiator-produced radicals. The ratio of rearranged products to unrearranged product increases with decreasing initial aldehyde concentrations. This concentration dependence has been used as evidence in establishing that two discrete radicals are involved in the rearrangement. Explanations are offered in interpreting the observed lack of rearrangement when 2-formyldibenzobicyclo[3.2.1.]octadiene is decarbonylated.

A C K N O W L E D G E M E N T S

I would like to thank my supervisor, Dr. D. D. Tanner, for his guidance of this study.

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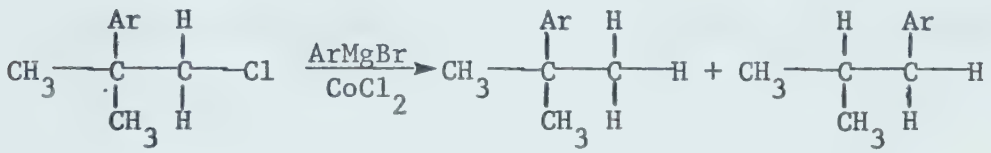
INTRODUCTION

In the relatively short history of free radical rearrangements, 1,2-phenyl shifts occupy an important place. In 1945, Kharasch, Lambert and Urry (1) reported such a rearrangement in the neophyl radical; it was the first demonstration of a carbon radical rearrangement in solution. Treatment of 1-chloro-2-methyl-2-phenylpropane (neophyl chloride) with phenylmagnesium bromide in the presence of cobaltous chloride led to a mixture of hydrocarbons in 55% yield, half of which had rearranged.



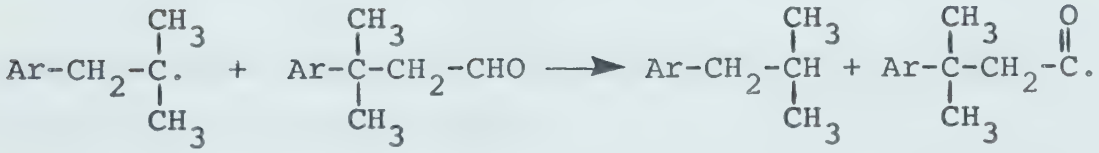
Accordingly, this type of 1,2 phenyl migration has become known as the neophyl rearrangement and has subsequently been observed in many other systems. Amongst these can be mentioned free radical additions to olefins (2), the decomposition of azo compounds (3), the thermolysis of peroxy compounds (4), the attack on alkyl benzenes by peroxides (5), radical halogenations (6), and the peroxide-induced decarbonylation of aldehydes (7). There are several reviews of the reaction; amongst them may be cited those by Walling (8), Freidlina (9) and Wilt (10).

The decarbonylation of aldehydes has proved to be a valuable reaction in the investigation of the neo-

phyl rearrangement. Winstein and Seubold (7a) investigated the decarbonylation of 3-methyl-3-phenylbutanal and found that the reaction, initiated by di-tert-butyl peroxide, gave, in 70% yield, approximately equal amounts of tert-butyl benzene and iso-butyl benzene. They proposed the following path;

a

b



Urry and Nicolaides (7b) showed that the rearrangement of a tertiary radical to a primary one (i.e. the reverse neophyl rearrangement) does not take place. They decarbonylated 2,2-dimethyl-3-phenyl propanal and found

that the products were derived from the unrearranged 1,1-dimethyl-2-phenylethyl radical. This action indicates that the higher stability of one of the radicals, usually the rearranged one, is a significant factor in the rearrangement.

However, a study by Slaugh (11) indicated that the higher stability of one of the radicals is not the sole reason for the rearrangement. Slaugh decarbonylated 3-phenylpropionic-2-^{14}C aldehyde to obtain 2-phenylethyl-1-^{14}C radicals, and found that these radicals undergo rearrangement as shown. The extent of rearrangement varied between 3.3 and 5.1%, depending on the temperature employed.

$$Ar\text{-}CH_2\text{-}^{14}CH_2\text{-}CHO \longrightarrow Ar\text{-}CH_2\text{-}^{14}CH_2\cdot$$

$$Ar\text{-}CH_2\text{-}^{14}CH_2\cdot \longrightarrow \cdot CH_2\text{-}^{14}CH_2\text{-}Ar$$

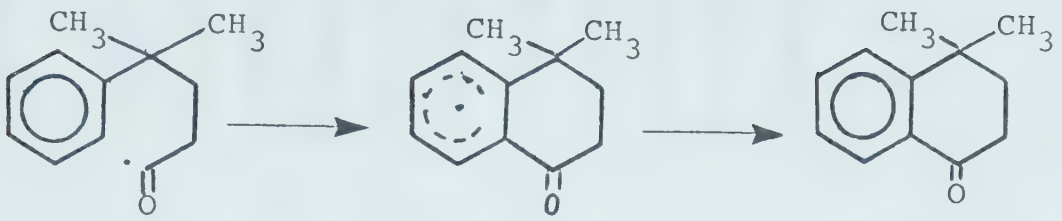
In this case, there are no structural factors which might favour rearrangement.

The factor which does indeed seem to affect the extent of rearrangement is the lifetime of the radicals involved. There have been several studies carried out which have shown that the extent of rearrangement upon decarbonylation of aldehydes decreases on addition of a hydrogen donor. Winstein, Heck, Lapporte and Baird

(12), Slaugh (11), and Wilt and Philip (7d) examined the decarbonylation of various aldehydes and showed that the extent of rearrangement decreases upon the addition of such donors as mercaptans. For example, Wilt and Philip (7d) showed that the addition of benzyl mercaptan to 1-phenylcyclohexylacetaldehyde inhibited the formation of rearranged product. The chain-transfer constants for mercaptans are considerably higher than those for aldehydes, and accordingly the addition of a mercaptan decreases the lifetime of radicals so that they are trapped before they rearrange.

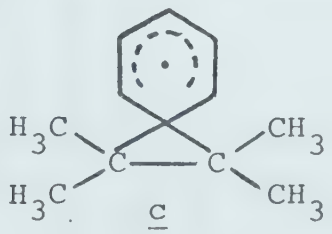
Where there is no chain-transfer agent added, rearrangement can be inhibited by decreasing the concentration of the reacting aldehyde. The higher the concentration of the aldehyde, the greater will be the trapping of the unrearranged decarbonylated radical by its chain transfer with unreacted aldehyde. Of course, the radicals can undergo other reactions, such as reaction with the solvent, disproportionation, coupling with each other and with radicals derived from the initiator. There is also the possibility of the formation of ketonic products from the radical initially produced by the abstraction of the aldehydic proton. For example, the peroxide-initiated reaction of 4-methyl-4-phenylpentanal at 100° gave 18% of 4,4-dimethyl-1-tetralone, which must have arisen by intramolecular

addition to the benzene ring by the initially formed radical (13).



All these possible reactions are exemplified in Scheme I by the decarbonylation of 3-methyl-3-phenylbutanal.

The mechanism of the neophyl rearrangement is widely assumed to involve two discrete radicals, the unrearranged and rearranged ones; bridged radicals are only involved as transition states or short-lived unstable intermediates. The evidence for this assumption is widespread. Kochi and Krusic (14) have failed in their attempt to detect the spiro radical, c, by electron paramagnetic resonance spectroscopy at low tempera-



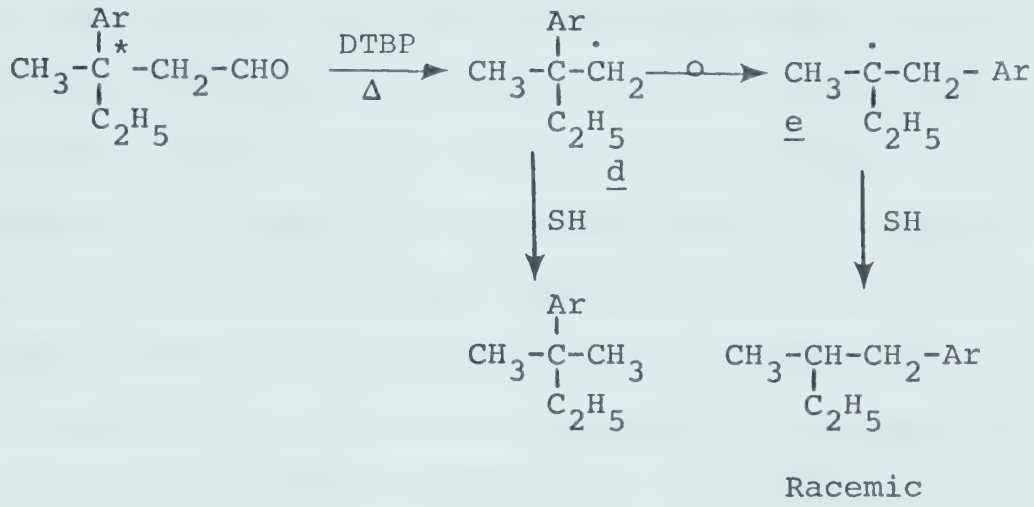
c

tures; they observed a spectrum corresponding to the open radical. Also, the extent of rearrangement is inversely dependent on substrate concentration (15) and is decreased if efficient chain transfer agents are present (7d). The decarbonylation of optically active

SCHEME I

i)	In	$\longrightarrow$ 2 In.	Initiation
ii)	In. + $ArC(CH_3)_2CH_2CHO$	$\longrightarrow$ InH + $ArC(CH_3)_2CH_2CO.$ (A)	
iii)	(A)	$\longrightarrow$ $ArC(CH_3)_2CH_2.$ (B) + CO	Decarbonylation
iv)	(B)	$\longrightarrow$ $.C(CH_3)_2CH_2Ar$ (C)	Rearrangement
v)	(B) + $ArC(CH_3)_2CH_2CHO$	$\longrightarrow$ $ArC(CH_3)_3$ + (A)	Propagation
vi)	(C) + $ArC(CH_3)_2CH_2CHO$	$\longrightarrow$ $HC(CH_3)_2CH_2Ar$ + (A)	Propagation
vii)	2 $.C(CH_3)_2CH_2Ar$	$\longrightarrow$ $(CH_3)_2C{=}CHAr$ + $CH(CH_3)_2CH_2Ar$	Disproportionation
viii)	In. + (B)	$\longrightarrow$ $ArC(CH_3)_2CH_2In$	Coupling
ix)	In. + (C)	$\longrightarrow$ $In\text{-}C(CH_3)_2CH_2Ar$	Coupling
x)	In. + (A)	$\longrightarrow$ $ArC(CH_3)_2CH_2CO\text{-}In$	Ketonic Coupling
xi)	2 (B)	$\longrightarrow$ $(ArC(CH_3)_2CH_2)_2$	Dimerization
xii)	2 (C)	$\longrightarrow$ $(C(CH_3)_2CH_2Ar)_2$	Dimerization
xiii)	(B) + (C)	$\longrightarrow$ $ArC(CH_3)_2CH_2C(CH_3)_2CH_2Ar$	Dimerization

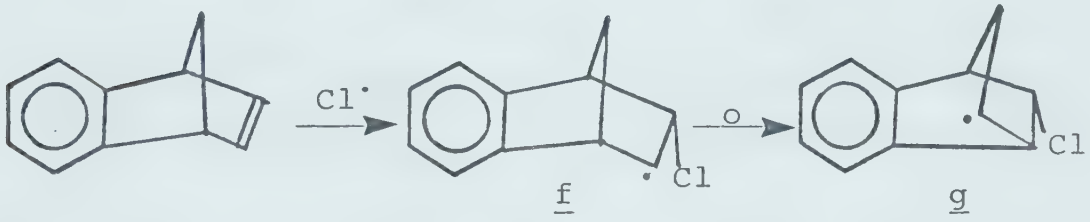
3-methyl-3-phenylpentanal gave racemic rearrangement product, whereas, had a bridged species been a product-forming intermediate, an inverted product would have been

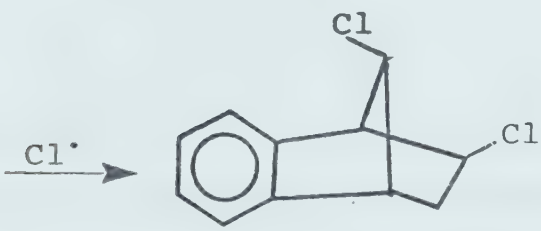


anticipated (16).

All these results indicate only that there are at least two discrete intermediates and it is still possible that one of these may be a bridged species. However, it is usually assumed that the two radicals are of the non-classical type. Evidence in support of this contention has been supplied by Hamilton and Fischer (17) who observed the low-temperature epr spectra of radicals a and b. They photolyzed tert-butylbenzene in the presence of di-tert-butyl peroxide and found that at low temperatures (below 270°K) only radical a was present. Above 360°K, only radical b was present and between these temperatures, both radicals were observed.

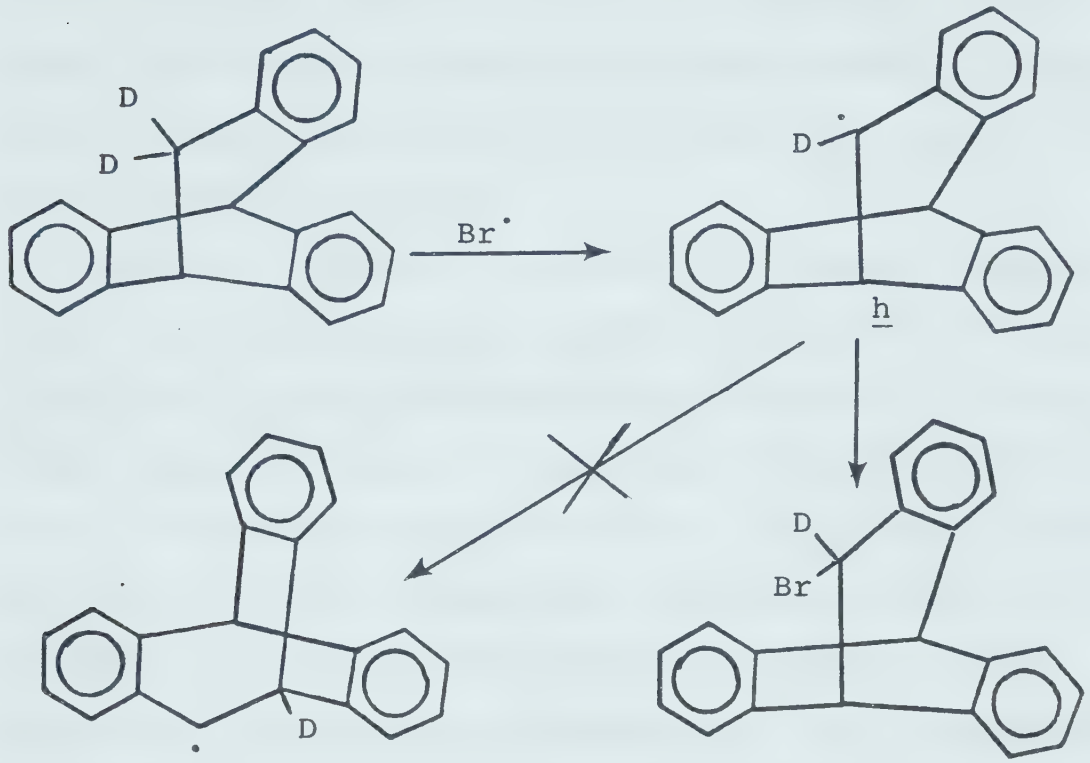
Free radical rearrangements have been observed in bicyclic systems. Cristol and Nachtigall (18) reported that the addition of chlorine atoms, produced from either nitryl or sulfuryl chloride, to benzonorbornadiene gave some exo-syn-dichloroide. Polar addition products were also found, and one of the criteria for ascribing the formation of the exo-syn-dichloride product to a radical pathway was that under polar conditions the initial attack was exo, whereas the formation of exo-syn-dichloride requires endo attack, such as is observed to the extent of 20% in the free radical bromination of norbornene (19).





Such radical rearrangements in the benzonorbornene system remain rare. Martin and Koster (20) did not observe any rearrangements in the radical addition of bromotrichloromethane, carbon tetrachloride or trichlorosilane to this

substrate. Cristol and Pennelle (21) found no rearrangement when 4,4-dideuteriotribenzobicyclo[3.2.2]nonatriene was brominated. They did find that the corresponding



cation rearranged.

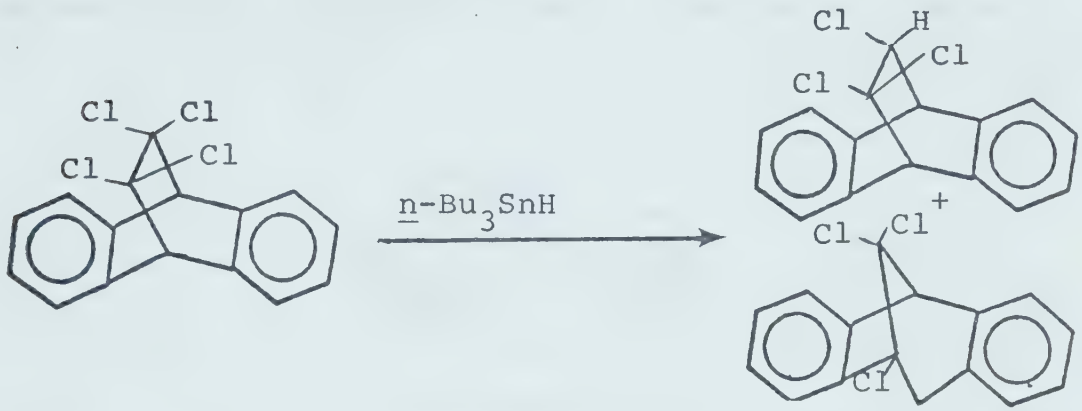
The paucity of instances of free-radical rearrangements in bicyclic systems led Tanner and Brownlee (22) to the conclusion that the formation of rearranged product in the iodination of dibenzobicyclo[2.2.2]octatriene was by an ionic pathway. Indeed, it seems likely that this was the case, since the reaction in the

absence of light yielded rearranged endo-4-syn-8-diiodo-dibenzobicyclo[3.2.1.]octadiene but upon irradiation trans-7,8-diiodibenzobicyclo[2.2.2.]octadiene was the only product formed. Iodine is a good transfer agent and it seems likely that the radical initially formed by addition of an iodine atom to the olefinic bond was trapped before it had time to rearrange.

Similarly, Cristol and Mueller (23) recently investigated the brominations of 7-methyldibenzobicyclo[2.2.2.]-octadiene, trans-7,8-dimethyldibenzobicyclo[2.2.2.]octadiene, cis-7,8-dimethyldibenzobicyclo[2.2.2.]octadiene and 7,7,8-trimethyldibenzobicyclo[2.2.2.]octadiene with bromine in carbon tetrachloride in the presence of light and they reported no rearrangement products of these reactions. This lack of rearrangement can be attributed to the rapid transfer of the radicals involved with bromine or with hydrogen bromide. The tertiary radical which was formed in each case would have been expected to have a longer lifetime than the substituted secondary radical at the same position and therefore, had the transfer not been so fast, rearrangement would have been possible.

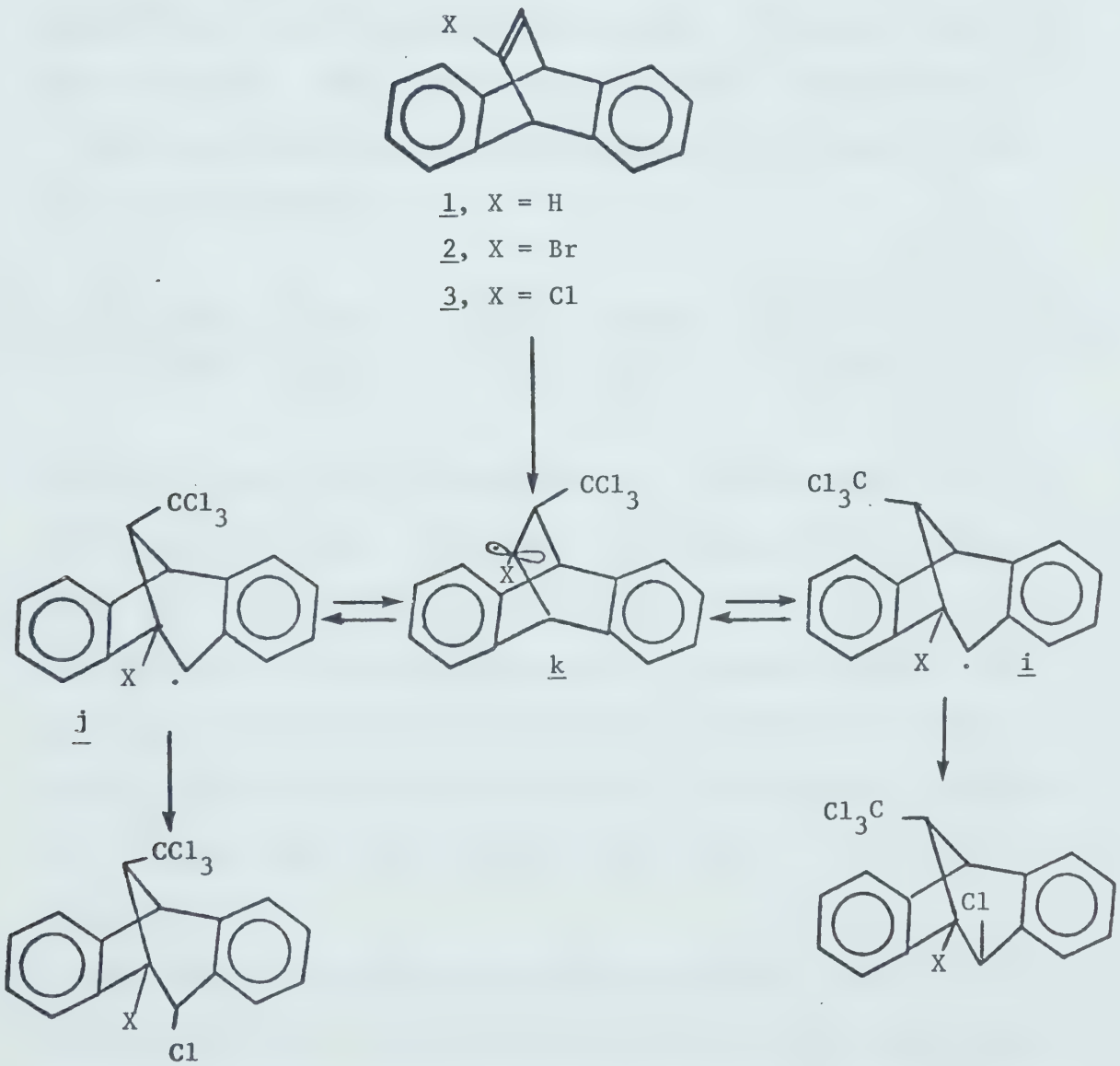
Recently, Jarvis and Yount (24) reported an example of a 1,2 phenyl migration in the dibenzobicyclo[2.2.2]-octadiene system. Carbonium ion rearrangements in this system are well known, but this was the first report

of a free radical rearrangement. The authors showed that the reduction of 7,7,8,8-tetrachlorodibenzobicyclo[2.2.2.]-octadiene by tri-n-butyl tin hydride led not only to 7,7,8-trichlorodibenzobicyclo[2.2.2.]octadiene, but also to the rearrangement product 1,8,8-trichlorodibenzobicyclo[3.2.1.]octadiene.



They ascribed this rearrangement to a longer-than-anticipated lifetime of the 7,7,8-trichlorodibenzobicyclo-[2.2.2.]octadien-8-yl radical because of difficult chain transfer occasioned by the adjacent gem-dichloro function. When 7,7,8-trichlorodibenzobicyclo[2.2.2.]octadiene was allowed to react with tri-n-butyl tin hydride, only unrearranged trans-7,8-dichlorodibenzobicyclo[2.2.2.]-octadiene was obtained. In this instance there is only one β-chloro substituent and so, it was rationalized, there is diminished steric inhibition to chain transfer. In a further study in this system, Jarvis, Govoni and Zell (25) report that in the free-radical addition of either carbon tetrachloride or bromotrichloromethane to either dibenzobicyclo[2.2.2.]octatriene, 1, or to one of

the halo-olefins 2 or 3, reversible rearrangement was observed. The reactions are shown schematically below. The authors concluded that rearrangement was taking place reversibly because the product from i gained more than that from j when the temperature was raised and when the concentrations of chain-transfer agent were lowered.



This reversible rearrangement is somewhat unexpected because the benzylic radical would be expected to be much more stable than the initially generated one.

These results can be explained in another, although unprecedented, way. If the radical initially formed by addition to the olefin were a σ radical, it would have tetrahedral geometry because of its sp^3 hybridization. As a consequence, two isomeric radicals could be formed initially, and these could rearrange or transfer at different rates. The processes are shown in Scheme II.

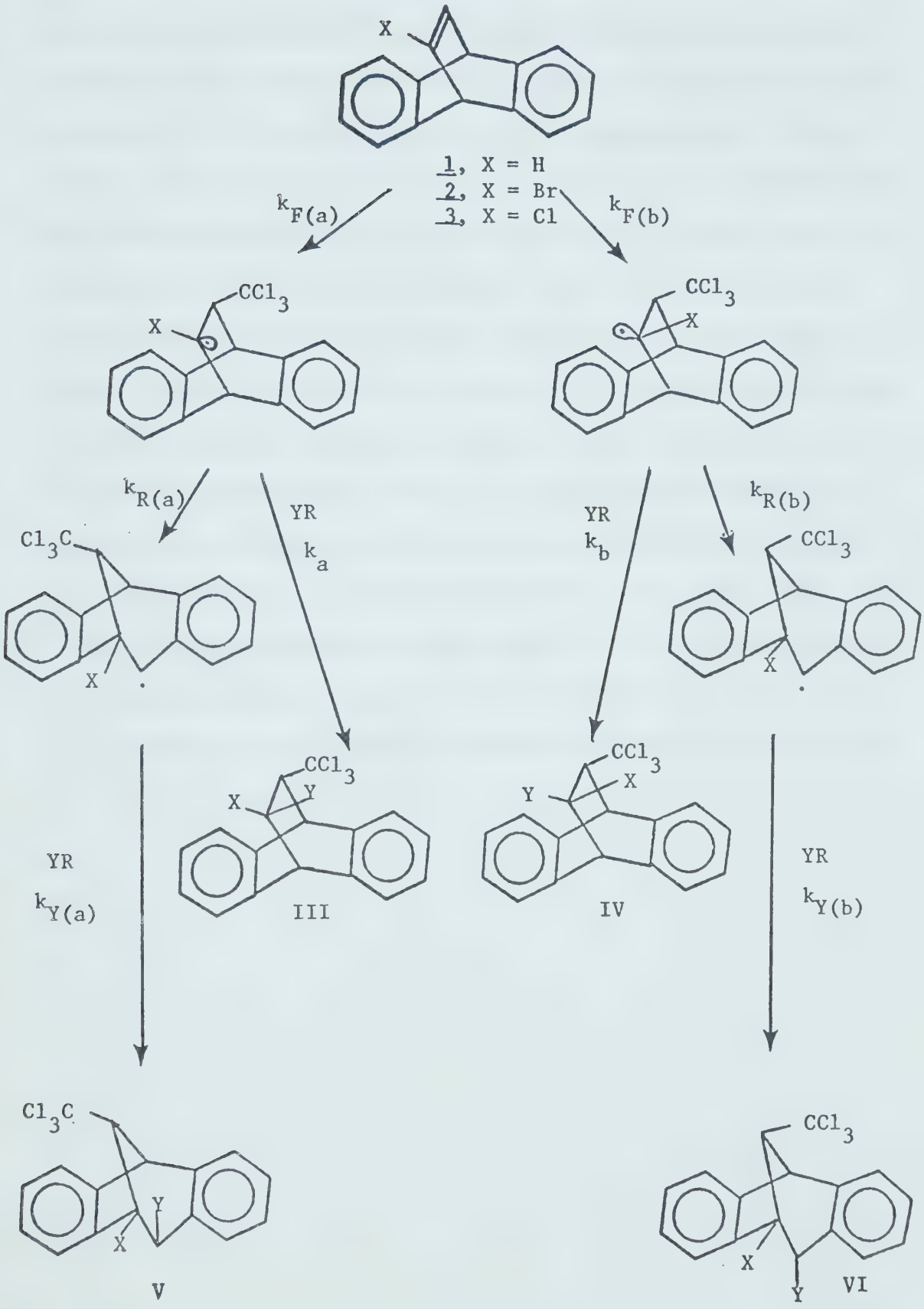
The rate equation for the formation of V and VI reduces to the form

$$\frac{d(V)/dt}{d(VI)/dt} = \frac{k_{R(a)}}{k_{R(b)}} \cdot \frac{k_{F(a)}}{k_{F(b)}} \frac{k_{R(b)} + k_{(b)}\,(YR)}{k_{R(a)} + k_{(a)}\,(YR)}$$

which is seen to be dependent upon the concentration of the transfer agent, YR. This mechanism also predicts that the ratio ((V) + (III))/((IV) + (VI)) would be independent of the concentration of transfer agent, YR; the reported results bear out this prediction. It must be stressed that this proposal of a tetrahedral radical is a speculative one, but one that merits further investigation.

To date, no studies have been reported where, in a bicyclic system, the equilibrium between the two radicals has been approached from both sides. Such a tandem

SCHEME II


X
1, X = H
2, X = Br
3, X = Cl
$k_{F(a)}$
$k_{F(b)}$
CCl_3
X
$k_{R(a)}$
$k_{R(b)}$
YR
k_a
k_b
Cl_3C
Y
III
IV
$k_{Y(a)}$
$k_{Y(b)}$
V
VI

study should permit more knowledge to be obtained concerning the neophyl rearrangement in bicyclic systems, especially in the realm of rearrangement from a benzylic radical to a secondary one, as was reported by Jarvis (25). For these reasons, it was decided to generate both the dibenzobicyclo[2.2.2.]octadien-7-yl radical and the dibenzobicyclo[3.2.1.]octadien-4-yl radical and by a study of the products formed, to ascertain the extent of rearrangement of each of them. To avoid any effects due to substituents, which were present in the studies by Jarvis, peroxide-initiated decarbonylation of the corresponding aldehydes was chosen as the mode of generation of the radicals. It was recognized, of course, that the presence of a chlorine substituent, as in the compounds studied by Jarvis, could possibly facilitate the rearrangement of the benzylic radical to the [2.2.2.] one.

R E S U L T S

For the decarbonylation studies, the two aldehydes 7-formyldibenzobicyclo[2.2.2.]octadiene, 4, and 2-formyldibenzobicyclo[3.2.1.]octadiene, 5, were required. Compound 4 was prepared by the Diels Alder reaction of anthracene and acrolein, following a method of Murahashi, Yuki and Kosai (26).

The choice of the synthetic route to 2-formyldibenzobicyclo[3.2.1.]octadiene, 5, was governed by the accessibility of an intermediate known to possess the required bicyclo[3.2.1.]skeleton. Initially an attempt was made to react the Grignard reagent of 4-chlorodibenzobicyclo-[3.2.1.]octadiene, 6, with either gaseous formaldehyde or paraformaldehyde to bring about the synthesis of a primary alcohol which could then be oxidized to the required aldehyde. It proved difficult to make the Grignard reagent from the chloride, but when finally it was made, it was found to be inert to attack by formaldehyde. Upon hydrolysis, only the hydrocarbon, dibenzobicyclo[3.2.1.]-octadiene, 7, was obtained. Further reactions of the Grignard reagent with carbon dioxide in either the solid or gaseous form were also unsuccessful and again hydrolysis resulted in the isolation of the hydrocarbon 7. As a consequence of these results, the attempted synthesis of the aldehyde 5 *via* the chloride 6 was abandoned.

A second synthetic route was established which used dibenzobicyclo[3.2.1.]octadien-2-one, 8, as the key intermediate. The ketone was obtained by the chromium trioxide/pyridine oxidation of a mixture of exo- and endo-dibenzobicyclo[3.2.1.]octadien-2-ols. Its physical and spectral properties were identical to those reported (27, 28). The mixture of alcohols was obtained by a sequence of reactions established by Cristol (27,30). The ketone was converted to the required aldehyde in poor yield by the Darzens reaction, or, in better yield, by the use of dimethylsulfoniummethylide.

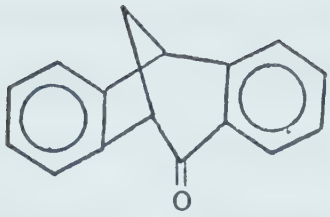
In the Darzens reaction the ketone was treated with ethyl chloroacetate and potassium tert-butoxide in tert-butanol to form the glycidic ester 9. The ester was not isolated but was treated with concentrated acid to yield the desired aldehyde in low yield, contaminated by unreacted ketone. A second technique, employing sodium ethoxide as the base, was even less successful. It had been hoped that it would prove possible to separate the aldehyde from the ketone by forming the sodium bisulfite adduct of the aldehyde, but the adduct could not be formed by either of the two procedures attempted (31,32). Chromatographic separation, employing either column or thick-layer techniques with a variety of solvents, was only partially successful as the ketone and the aldehyde had almost the same Rf values under these conditions.

Consequently, it was decided to try an alternative route to the desired aldehyde 5.

The second route, Route b, involved a reaction developed by Corey and Chaykovsky (33). The dimethylsulfoniummethylide was prepared by the reaction of n-butyl lithium on trimethylsulfonium iodide at low temperature. When this was added to a solution of the ketone, 8, also at low temperature, the epoxide 10 was formed. This was then treated with boron trifluoride etherate to yield the desired aldehyde as a mixture of presumably the exo and endo isomers. Once again there was present unreacted starting ketone, but in this case the proportion of aldehyde to ketone was significantly greater. A column chromatography partial separation of the aldehyde from the ketone yielded a mixture of 90:10% of aldehyde to ketone. Since the ketone was shown not to react under the conditions of the decarbonylation reactions, and since the proportion of ketone to aldehyde could be determined by glpc, it was this mixture which was used in the decarbonylation studies.

Peroxide-Initiated Decarbonylation of 7-Formyldibenzobicyclo[2.2.2.]octadiene

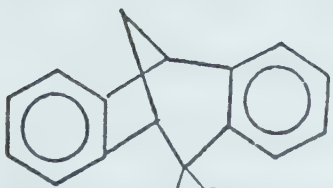
The initial study was carried out upon 7-formyldibenzobicyclo[2.2.2.]octadiene, 4, in the presence of benzoyl peroxide as a free radical initator. It was



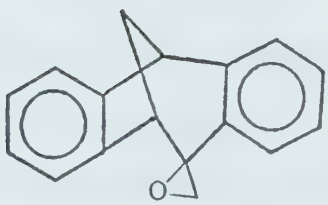
8

(a) $(CH_3)_3CO^-K^+/(CH_3)_3COH$, $ClCH_2COOEt$

(b) $\bar{C}H_2-\overset{+}{S}(CH_3)_2$



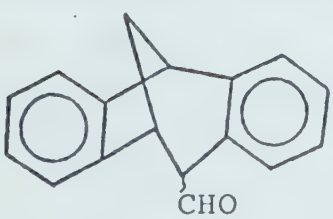
9



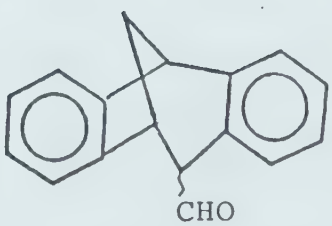
10

HCl

$BF_3.Et_2O$



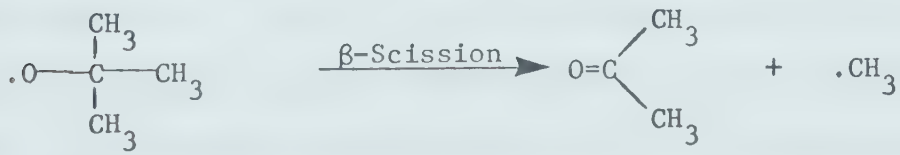
5



5

found that dibenzobicyclo[2.2.2.]octadiene, 11, and dibenzobicyclo[3.2.1.]octadiene, 7, arising from the unrearranged and rearranged radicals, were, indeed, among the products. However, there was such a plethora of other products formed which appeared to arise from the initiator and which were difficult to identify and separate that it was decided to change the initiator. Accordingly, all subsequent experiments were carried out using as free radical initiator tert-butyl perpivalate, which was prepared by the reaction of pivaloyl chloride with tert-butyl hydroperoxide. Chlorobenzene was chosen as solvent for the decarbonylations since it is known to be relatively inert to free radical attack (34).

Preliminary studies with this initiator showed that once again the two hydrocarbons 7 and 11 were formed. However, they were not the only compounds produced in the reaction. Various coupling products were also observed. At the temperatures employed in the decarbonylations, tert-butyl perpivalate gives rise to tert-butyl, tert-butoxy and methyl radicals (35).



Any of these radicals may react by either abstraction, addition or coupling with the substrate or with either of the radicals which arise from its decarbonylation. They may, of course, couple with each other, but only anthracene and those products which contained either the dibenzobicyclo[2.2.2.]octadiene skeleton or the dibenzobicyclo[3.2.1.]octadiene skeleton were considered in the analysis of the reaction products. Under the conditions of analysis, these initiator-derived products were eluted before the external standard and were not resolved. Because of the short chain lengths in decarbonylation reactions (36), a relatively high concentration (0.15 M) of initiator was necessary to achieve a significant amount of reaction.

If all the possible combinations of the radicals derived from the initiator (methyl, tert-butyl and tert-butoxy) and the rearranged and unrearranged dibenzobicyclo radicals are considered, a total of nine radical coupling products are possible, since the rearranged dibenzobicyclo products can be formed with either exo or endo stereochemistry. There is also the possibility of coupling between two dibenzobicyclo radicals and these reactions would in theory give rise to a further five products. Of all these products, the following were found: exo-4-tert-butyldibenzobicyclo[3.2.1.]octadiene, 12, 4-methyldibenzobicyclo[3.2.1.]octadiene, 13,

(the stereochemistry of this product was not established), exo-2-tert-butoxydibenzobicyclo[3.2.1.]octadiene, 14, and endo-2-tert-butoxydibenzobicyclo[3.2.1.]octadiene, 15. The first of these was a major product (>70% of coupling products), whereas the latter three were minor (each less than 2% of the yield of total products). Additionally, there was evidence that endo-4-tert-butyldibenzobicyclo-[3.2.1.]octadiene, 16, was also present in a minor amount (<4% of total products). Evidence also existed for the assignment of another minor peak in the glpc analysis trace to 4-bis-(dibenzobicyclo[3.2.1.]octadiene), 17; this compound would have arisen from coupling between two of the rearranged radicals. It was a minor product (<3% of total products). The radical coupling products formed from 42% to 64% of the total yield of products.

Not all of these compounds were independently synthesized; however, the two ethers 14 and 15 (and also 7-tert-butoxydibenzobicyclo[2.2.2.]octadiene, 18, which was not a reaction product), were prepared by the reaction of the corresponding alcohol with isobutylene in the presence of acidic resin. None of the three hydrocarbons 12, 13 and 16 was prepared but, for the purposes of comparison of their spectral properties and glpc retention times, their [2.2.2.] analogues were. 7-Methyldibenzobicyclo[2.2.2.]octadiene, 19, a known

compound (37), was obtained by the Clemmensen reduction of 7-formyldibenzobicyclo[2.2.2.]octadiene; the yield was small but the route had the advantage of confirming the structure of the aldehyde. 7-tert-Butyldibenzobicyclo-[2.2.2.]octadiene, 20, was prepared by the Diels Alder reaction of anthracene and 3,3-dimethyl-1-butene. Even though forcing conditions were used, the yield was small, but there was no other obvious route to this compound which would not have involved the possibility of the formation of a carbonium ion or a free radical at the 7-position.

In the preliminary study using benzoyl peroxide as initiator, there was found 7-carboxydibenzobicyclo[2.2.2.]-octadiene, 21, the acid corresponding to the oxidation product formed by oxidation of the starting aldehyde 4. It is possible that this contaminant was a result of air oxidation of the aldehyde. Certainly this process takes place, as evidenced by the presence of the acid in an erstwhile uncontaminated sample of aldehyde 4 which had been allowed to remain in contact with the air for several weeks. In view of this, all batches of aldehyde 4 were routinely subjected to infrared analysis before decarbonylation in order to ensure that they were free of acid contamination. After this precautionary measure was instituted, no 7-carboxydibenzobicyclo[2.2.2.]octa-diene was observed in the analyses of the reaction mix-

tures. For comparison, an authentic sample of 7-carboxydibenzobicyclo[2.2.2.]octadiene, 21, was obtained by the silver-oxide oxidation of 7-formyldibenzobicyclo[2.2.2.]-octadiene.

The glpc analyses of the product mixtures were carried out using a liquid phase of neopentyl glycol succinate (NPGS) on acid-washed Chromasorb P, 60-80 mesh. Two columns of this packing material were employed in the analyses. Under isothermal conditions at 150°, a 4 ft x 0.25 in NPGS column was able to separate the external standard (biphenyl), the two isomeric hydrocarbons 11 and 7, dibenzobicyclo[2.2.2.]octatriene, 1, 7-methyldibenzobicyclo[2.2.2.]octadiene, 19, 4-methyldibenzobicyclo-[3.2.1.]octadiene, 13, anthracene, 22, 7-tert-butyldibenzobicyclo[2.2.2.]octadiene, 20, and exo-4-tert-butyldibenzobicyclo[3.2.1.]octadiene, 12. Under the same temperature conditions a 2 ft x 0.25 in NPGS column was able to separate the external standard, exo-4-tert-butyldibenzobicyclo[3.2.1.]octadiene, 12, endo-4-tert-butyldibenzobicyclo[3.2.1.]octadiene, 16, 7-tert-butoxydibenzobicyclo[2.2.2.]octadiene, 18, exo-2-tert-butoxydibenzobicyclo[3.2.1.]octadiene, 14, endo-2-tert-butoxydibenzobicyclo[3.2.1.]octadiene, 15, the presumed bis-4-(dibenzobicyclo[3.2.1.]octadiene), 17, 7-formyldibenzobicyclo[2.2.2.]octadiene, 4, and 7-carboxydibenzobicyclo-[2.2.2.]octadiene, 21.

Typical chromatographic traces are shown in Figures I and II.

Quantitative Studies on the Decarbonylation of 7-Formyl-dibenzobicyclo[2.2.2.]octadiene

Weighed amounts of the aldehyde were placed in thick-walled Pyrex ampoules, followed by an aliquot of a standard solution of tert-butyl perpivalate in chlorobenzene. After being degassed by the freeze-thaw method and sealed, the ampoules were placed in an oil bath thermostated to 84° for a time of at least ten half-lives of the initiator. Upon completion of the reaction the ampoules were removed from the bath, frozen and opened. An aliquot of a standard solution of biphenyl in chlorobenzene was added. The reaction mixtures were then analysed by glpc as was described above. The results of these experiments are shown in Table I. The concentrations of the starting aldehyde 4 were varied in order to investigate whether the ratios of the dibenzobicyclo[2.2.2.]-octadiene to dibenzobicyclo[3.2.1.]octadiene were dependent upon the initial concentration of the starting aldehyde. These ratios were found to increase from 0.613 to 7.68 as the concentrations of the aldehyde 4 dropped from 8.22×10^{-1} M to 5.08×10^{-2} M. A more significant ratio is one which compares the total amount of products with the [2.2.2.]skeleton with the total

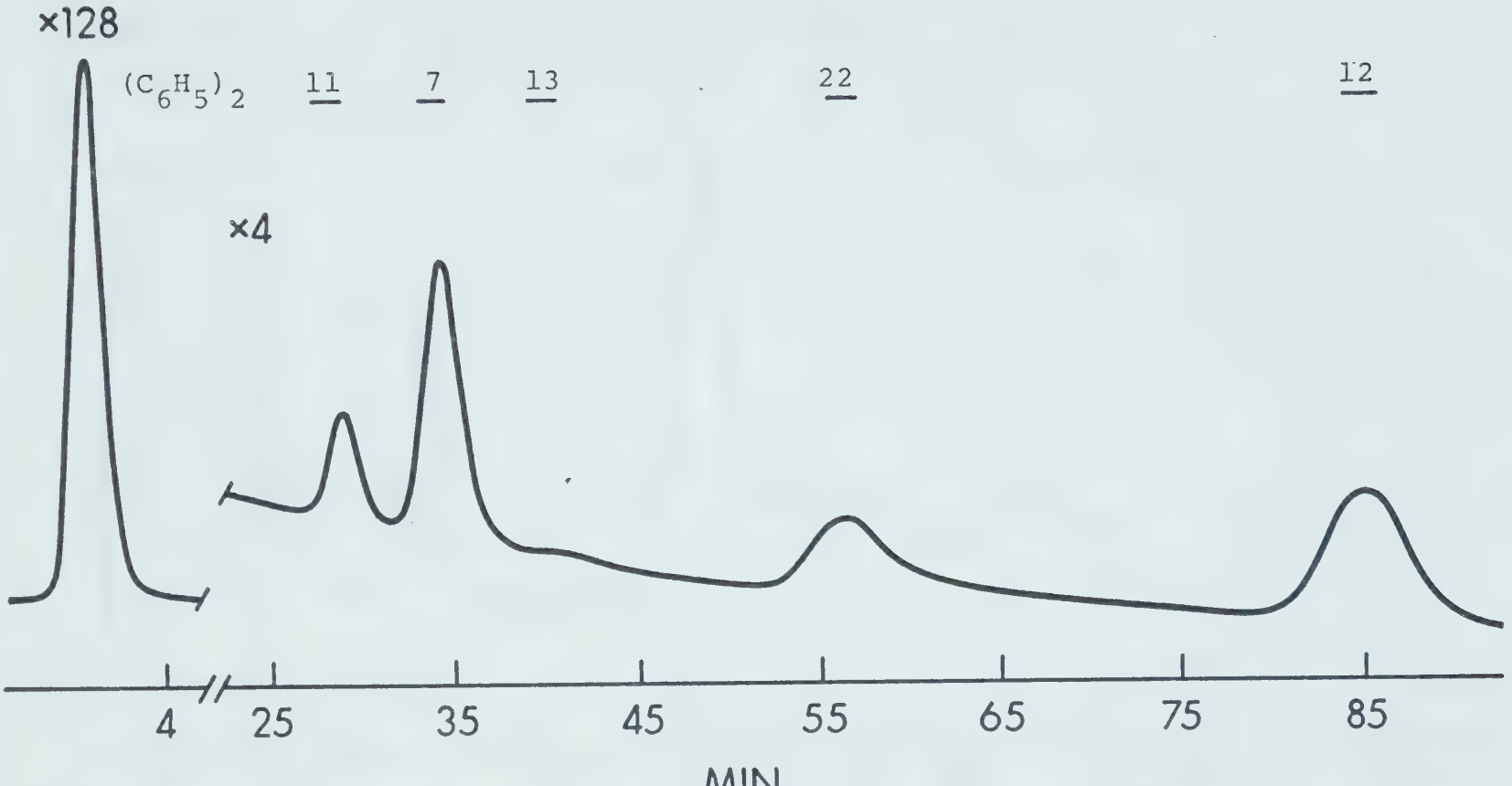


FIGURE I Analysis of Reaction of 7-Formyldibenzobicyclo[2.2.2.]octadiene at 150°, 4 ft NPGS

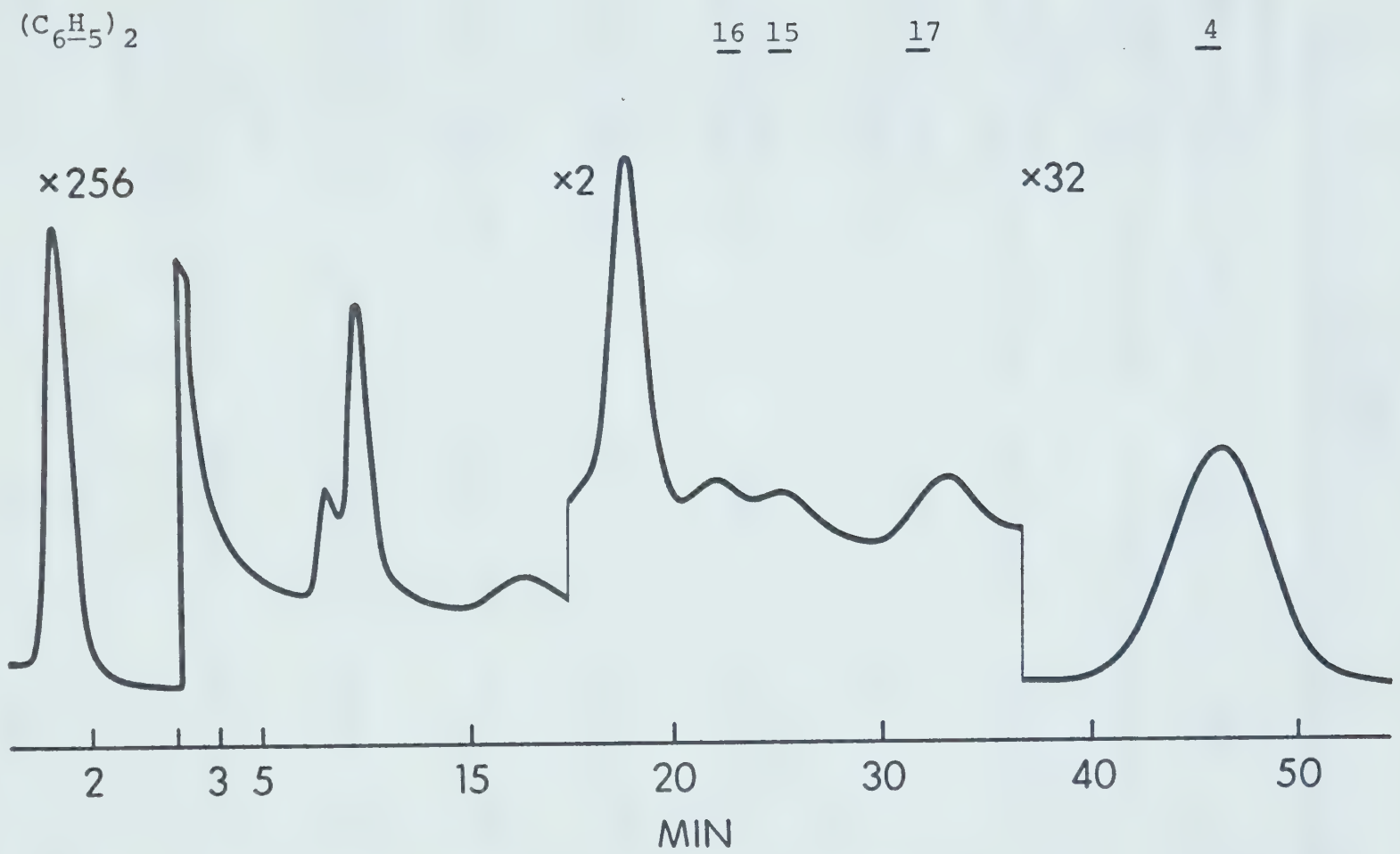
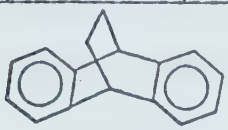
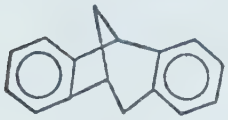
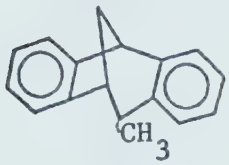
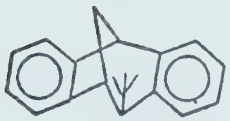
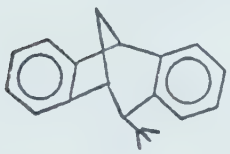
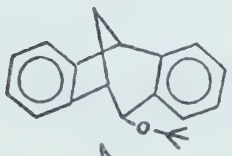
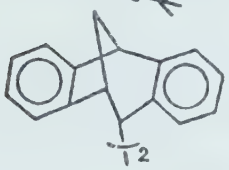
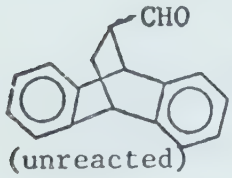


FIGURE II. Analysis of Reaction of 7-Formyldibenzobicyclo[2.2.2.]octadiene at 150°, 2 ft NPGS

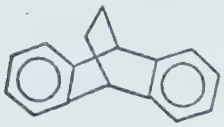
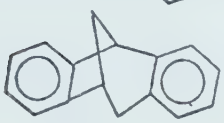
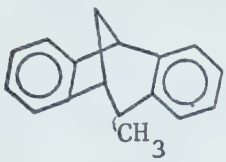
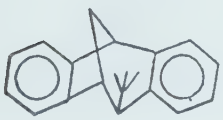
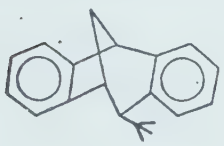
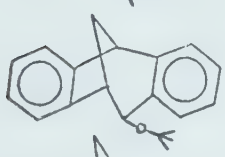
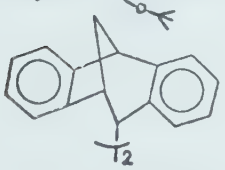
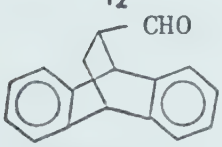
TABLE I

Reaction of 7-Formyldibenzobicyclo[2.2.2.]octadiene at 84°

Reaction	1	2	3	4
$\frac{4}{}$ (mole x 10^6)	850	363	310	290
	7.63 ± 0.02*	3.87 ± 0.02	3.04 ± 0.01	3.04 ± 0.05
	4.68 ± 0.07	3.92 ± 0.03	4.28 ± 0.03	4.23 ± 0.02
	0.0	0.0	0.0	0.05 ± 0.002
	0.64 ± 0.06	1.81 ± 0.2	2.95 ± 0.02	3.07 ± 0.08
	0.0	0.0	0.24 ± 0.006	0.23 ± 0.006
	3.47 ± 0.15	0.79 ± 0.01	0.26 ± 0.007	0.29 ± 0.01
	1.42 ± 0.08**	0.76 ± 0.03**	0.68 ± 0.01**	0.77 ± 0.01**
 (unreacted)	846 ± 0.7	339 ± 0.01	277 ± 0.1	240 ± 0.1
Total products (mole x 10^6)	865	350	289	252
Material Balance	102%	96.3%	93.2%	86.8%
[3.2.1.] product / [2.2.2.] product	1.52	2.08	3.00	3.10

(continued.....)

TABLE I (continued)

Reaction	5	6	7
4 (mole x 10^6)	239	139	52.6
Products (mole x 10^6)			
	2.24 ± 0.01*	1.23 ± 0.02	0.37 ± 0.01
	3.78 ± 0.01	3.78 ± 0.02	2.83 ± 0.01
	0.08 ± 0.001	0.08 ± 0.001	0.20 ± 0.005
	2.92 ± 0.03	3.94 ± 0.03	2.88 ± 0.01
	0.24 ± 0.004	0.39 ± 0.003	0.35 ± 0.002
	0.25 ± 0.006	0.55 ± 0.002	0.98 ± 0.03
	0.09 ± 0.0005**	1.07 ± 0.01**	1.26 ± 0.03**
 (unreacted)	201 ± 0.1	80.0 ± 0.03	8.50 ± 0.06
Total products (mole x 10^6)	211	92	18
Material Balance	88%	68%	35%
[3.2.1.]product / [2.2.2.]product	3.33	8.86	26.55

(continued.....)

FOOTNOTES TO TABLE I

* Average deviation from the mean of three glpc analyses.

** In the calculation of the material balance, these quantities have been doubled.

amount of products with the [3.2.1.]skeleton. It is in this form that the results are reported in Table I (Reactions 1 to 7).

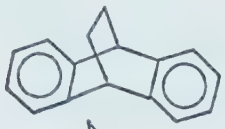
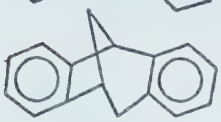
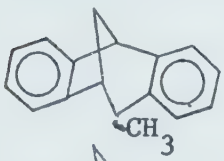
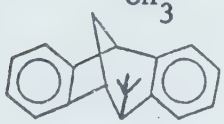
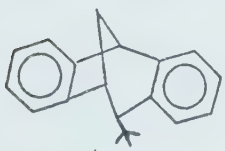
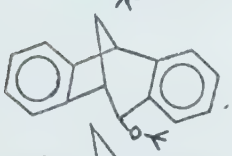
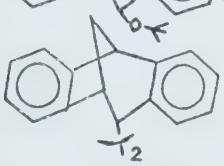
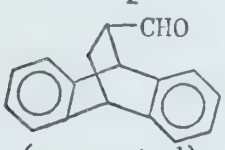
For the high-temperature decarbonylation study the oil bath temperature was raised to 120°. In all other respects, the conditions of reaction and analysis were the same as those above. The result is shown in Table II (Reaction 8).

Decarbonylation of a Mixture of exo- and endo-2-Formyldibenzobicyclo[3.2.1.]octadiene

Since these aldehydes were not obtained in appreciable amounts completely free of their precursor dibenzobicyclo[3.2.1.]octadien-2-one, the impure sample was first analyzed by glpc to determine the relative amounts of each component in the mixture. Then weighed amounts of this mixture were placed in thick-walled Pyrex ampoules, followed by an aliquot of a standard solution of the initiator in chlorobenzene, and the same procedure was followed as was described above. The reaction mixtures were analyzed by glpc; because the substrate aldehydes did not undergo a retro-Diels Alder reaction on the column, it was possible to raise the temperature of the column and so analyze the mixtures on 4 ft x 0.25 in NPGS alone. The results are given in Table III (Reactions 9 and 10). A typical chromatogram is shown in Figure III.

TABLE II

Reaction of 7-Formyldibenzobicyclo[2.2.2.]octadiene at 120°

Reaction	8
4 (mole x 10^6)	62.0
Products (mole x 10^6)	
	0.30 ± 0.006*
	3.86 ± 0.04
	0.60 ± 0.01
	4.35 ± 0.02
	0.73 ± 0.03
	0.37 ± 0.004
	0.46 ± 0.002**
 (unreacted)	20.00 ± 0.07
Total products (mole x 10^6)	30.7
Material Balance	49%
[3.2.1.]product / [2.2.2.]product	37.89

(continued.....)

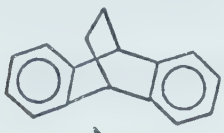
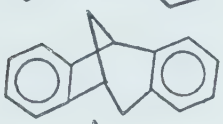
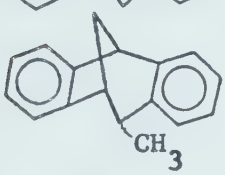
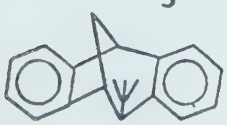
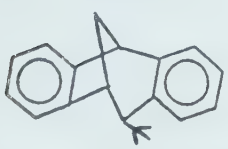
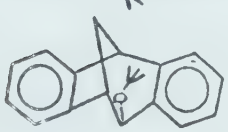
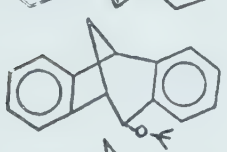
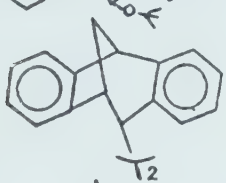
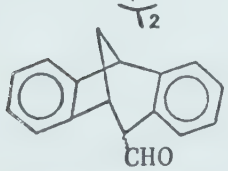
Footnotes to Table II

* Average deviation from the mean of three glpc analyses.

** In the calculation of the material balance, this quantity has been doubled.

TABLE III

Reaction of 2-Formyldibenzobicyclo[3.2.1.]octadiene at 84°

Reaction	9	10
5 (mole x 10^6)	391	72.0
Products (mole x 10^6)		
	0.0	0.0
	4.30 ± 0.02*	2.23 ± 0.04
	0.05 ± 0.001	0.07 ± 0.002
	0.39 ± 0.007	2.12 ± 0.01
	0.04 ± 0.0001	0.19 ± 0.01
	0.03 ± 0.0001	0.17 ± 0.002
	1.39 ± 0.07	0.56 ± 0.008
	0.41 ± 0.007**	0.18 ± 0.008**
 (unreacted)	3.44 ± 0.01	25.4 ± 0.3
Total products (mole x 10^6)	350	31
Material Balance	90%	43%

(continued.....)

FOOTNOTES TO TABLE III

* Average deviation from the mean of three glpc analyses.

** In the calculation of the material balance, these quantities have been doubled.

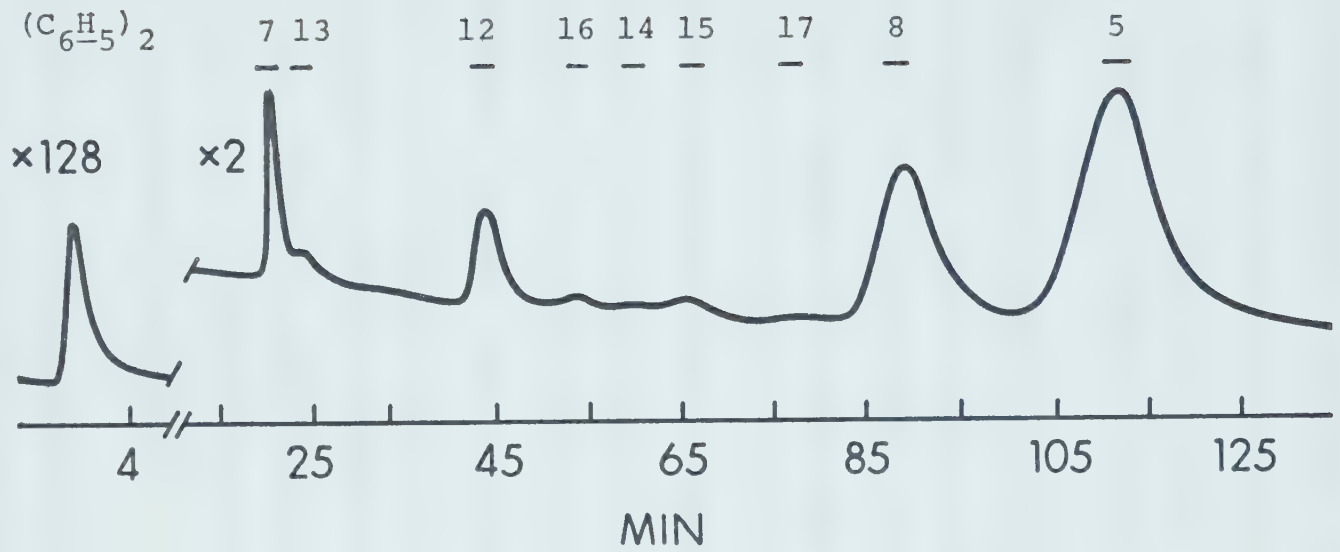


FIGURE III Analysis of Reaction of 2-Formyldibenzobicyclo[3.2.1.]octadiene at 175°, 4 ft NPGS

For the high-temperature decarbonylation study, the oil bath temperature was raised to 120°. In all other respects, the conditions of reaction and analysis were the same as those immediately above. The result of this analysis is shown in Table IV (Reaction 11).

Identification of the Products of the Reactions

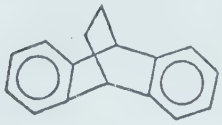
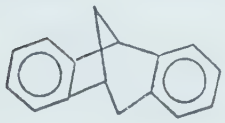
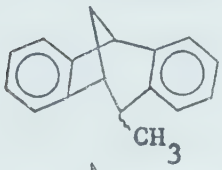
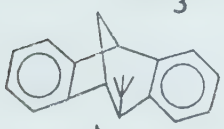
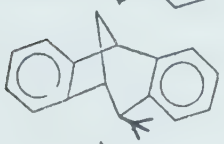
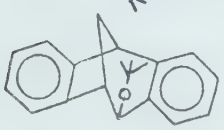
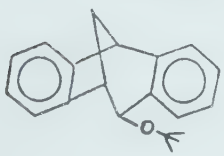
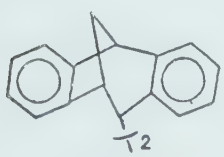
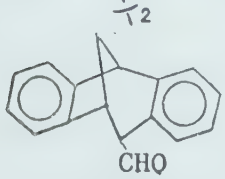
The compounds corresponding to the peaks on the glpc chromatogram were individually collected by preparative glpc and were purified by reinjection and recollection. Their mass spectra, infrared spectra, and, where possible, their Fourier Transform Proton Magnetic Resonance spectra were obtained. These were compared with those of authentic materials, or, where this was not possible, with close analogues. Where authentic materials were available, the glpc retention times were compared after the addition of these authentic materials to the collected products and with subsequent reanalysis by glpc. Two columns were used to compare the retention time of each compound in the reaction mixture.

Thermal Stabilities of Starting Materials and Products

It was necessary to determine the thermal stabilities of the starting aldehydes 4 and 5 and of the free-radical decomposition products, dibenzobicyclo[2.2.2]-octadiene, 11, and dibenzobicyclo[3.2.1.]octadiene, 7. The two hydrocarbons and the [3.2.1.] aldehyde 5 proved

TABLE IV

Reaction of 2-Formyldibenzobicyclo[3.2.1.]octadiene at 120°

Reaction	11
5 (mole x 10^6)	32.0
Products (mole x 10^6)	
	0.0
	1.04 ± 0.03*
	0.25 ± 0.006
	0.68 ± 0.001
	0.15 ± 0.003
	0.24 ± 0.001
	0.39 ± 0.004
	0.57 ± 0.002**
 (unreacted)	4.83 ± 0.03
Total products (mole x 10^6)	8.8
Material Balance	28%

(continued.....)

FOOTNOTES TO TABLE IV

* Average deviation from the mean of three glpc analyses.

** In the calculation of the material balance this quantity has been doubled.

to be stable thermally, and the two hydrocarbons were also stable to the reaction conditions. However, the [2.2.2.] aldehyde 4 underwent a retro-Diels Alder reaction to a certain extent, as evidenced by the production of anthracene during the analysis by glpc. It was found that the use of a glass column and a glass-lined detection system minimized this problem. Column temperatures were also critical; above 180°, the retro-Diels Alder reaction became significant, and at temperatures between 140° and 180° the reaction still occurred but at an appreciably lower level. Below 140° the column reaction was unobservable; however, the low temperature made elution times exceedingly long. Analysis of the reaction mixtures at this lower temperature showed that no anthracene was formed during the reaction and was only an artifact of this analysis. Since only 7-formyl-dibenzobicyclo[2.2.2.]octadiene, 4, gave anthracene on analysis, this amount of anthracene which formed was added to the amount of unreacted aldehyde 4 in Tables I and II. The [3.2.1.] aldehyde 5 did not undergo any decomposition during the analysis, and neither did the ketone 8.

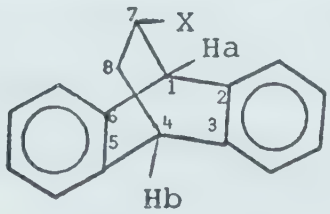
All the synthesized materials, with the exception of the carboxylic acid 21, were found to be stable to the reaction conditions and glpc analysis conditions.

The carboxylic acid 21, like the [2.2.2.] aldehyde 4, also underwent a retro-Diels Alder reaction under the conditions of analysis, but to a much lesser extent: ca. 1% with a column temperature of 150°. exo-4-tert-Butyldibenzobicyclo[3.2.1.]octadiene, 13, which was not synthesized, was collected by preparative glpc, and by reinjection was shown to be stable.

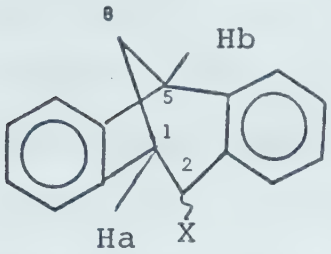
DISCUSSION

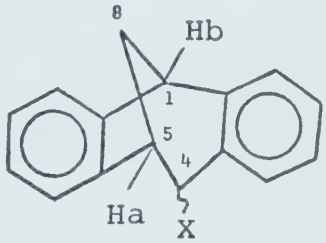
The decarbonylation of the isomeric aldehydes 7-formyldibenzobicyclo[2.2.2.]octadiene, 4, and 2-formyldibenzobicyclo[3.2.1.]octadiene, 5, was undertaken to study the extent of radical rearrangement in these bicyclic systems and to gain some insight into the nature of the intermediate or intermediates involved in the reaction. Because the mode of generation was the peroxide-initiated decarbonylation of the aldehydes, various radical coupling products were found in the reaction mixture, along with the expected dibenzobicyclo[2.2.2.]octadiene, 11, (when the [2.2.2.] aldehyde was decarbonylated) and dibenzobicyclo[3.2.1.]octadiene, 7. All but three minor products were identified positively and for these three, which comprised less than 5% of the total moles of product, the skeletal type was ascertained.

Whilst most of the compounds isolated were previously unknown, they were in all instances members of systems which have been extensively studied by nmr (28,29). The compounds with the dibenzobicyclo[2.2.2.]octadiene skeleton were all substituted on the bridge at the 7-position.



Compounds with the dibenzobicyclo[3.2.1.]octadiene skeleton were all substituted at the benzylic position (at the position numbered as 2 or 4, depending upon the priority assigned to the substituent).





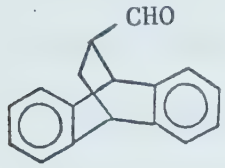
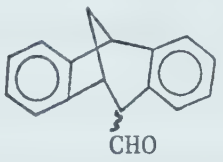
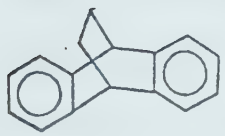
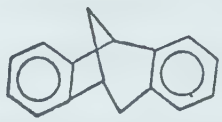
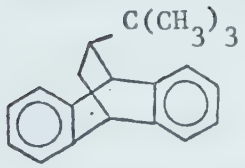
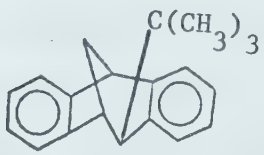
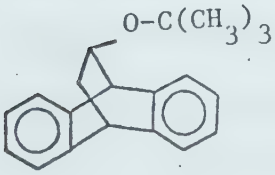
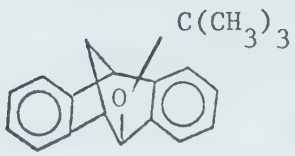
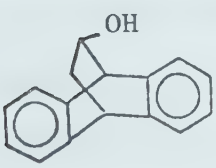
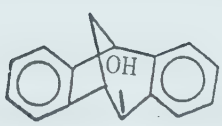
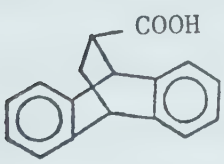
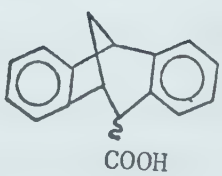
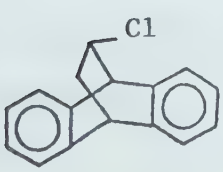
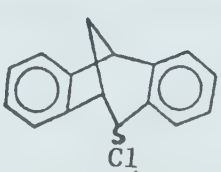
The characteristic aliphatic proton chemical shifts of members of each of the ring systems are sufficiently different to allow a distinction to be made between the two skeletal types. For example, the bridgehead proton nearer the substituent (proton 'a') and the bridgehead proton further from the substituent (proton 'b') have characteristic chemical shifts which are different in the two ring systems. For a variety of compounds (X = -OH, -Cl, $-NH_2$, -OAc, $-SC_6H_5$) in the [2.2.2.] system, proton a absorbs in the region τ 5.5 - 6.1 and appears as a doublet coupled to the proton geminal to the substituent, X, with a coupling constant of the order 2.5 Hz (29), whereas in the [3.2.1.] system, proton a usually absorbs in the region τ 6.4 - 6.6 (X = -OH, -Cl, -OAc). Similarly, the other bridgehead proton, b, absorbs in

the region of τ 5.7 - 5.9 in the [2.2.2.] system (X = -OH, -Cl, $-NH_2$, -OAc, $-SC_6H_5$), and appears as a triplet coupled to the two geminal bridge protons with a coupling constant in the range 2.5 - 3.0 Hz. In the [3.2.1.] system, proton b absorbs in the region τ 6.1 - 6.2 (X = -OH, -Cl, -OAc). Further, Cristol (28) has found that the coupling constant between the endo-benzylic proton (for exo substituted compounds) and proton a is 1.8 ± 0.5 Hz for twelve examples, and the coupling constant between the exo-benzylic proton (for endo substituted compounds) and proton a is 5.1 ± 0.5 Hz for seven examples.

Perhaps the least equivocal evidence as to the nature of the skeleton present in a particular product was given by mass spectroscopy. In the compounds studied whose structure was known, it was found that compounds with the dibenzobicyclo[2.2.2.]octadiene structure had a very strong peak corresponding to m/e 178 (molecular weight of anthracene is 178). This presumably resulted from fragmentation by a retro-Diels Alder-type of process whereby the bridge and its substituent was lost. The peak corresponding to m/e 205 (molecular weight of dibenzobicyclo[2.2.2.]octadiene is 206) was usually small. In contrast, compounds of the [3.2.1.] system were not able to lose the bridge in the same manner and so gave a strong peak corresponding to m/e 205 or 204, but a weak peak at m/e 178. In Table V the ratios of the magnitudes,

TABLE V

Ratios of Mass Spectra Intensities for Selected Dibenzobicyclo[2.2.2.]- and [3.2.1.]octadienes

[2.2.2.] isomer	m/e 178/205	[3.2.1.] isomer	m/e 178/205
	67		0.25
	67		0.37
	83		0.50
	29		0.13
	200		0.11
	67		0.29
	11		0.21

expressed as percentages of the base peak, of peaks of m/e 178 to 205 are given. It was felt reasonable to extrapolate these data to compounds whose structures were not known exactly but which were present in sufficient quantity to enable mass spectra to be obtained.

One additional, though not a spectral, trend was noted. During gas-liquid partition chromatographic (glpc) analysis of the reaction products and of known compounds, it was found that under the conditions of analysis employed, and using neopentyl glycol succinate (NPGS) as the liquid phase, a compound of the dibenzobicyclo[2.2.2.]octadiene series was always eluted before its [3.2.1.] isomer. Thus, dibenzobicyclo[2.2.2.]-octadiene came before dibenzobicyclo[3.2.1.]octadiene, 7-tert-butyldibenzobicyclo[2.2.2.]octadiene before 4-tert-butyldibenzobicyclo[3.2.1.]octadiene, 7-tert-butoxydibenzobicyclo[2.2.2.]octadiene before either exo- or endo-2-tert-butoxydibenzobicyclo[3.2.1.]octadiene, and 7-formyldibenzobicyclo[2.2.2.]octadiene before 2-formyldibenzobicyclo[3.2.1.]octadiene. Whilst it would have been incautious to use elution time as the sole criterion of isomeric structure, had a compound which had been assigned, say, the [3.2.1.] structure been eluted before its isomer of known [2.2.2.] structure, a cause for concern would have arisen. This never happened.

In the structure assignments of the products the spectral and glpc evidence was considered, along with elemental analyses where possible and comparison of spectra with those of authentic samples where available. When authentic compounds were not available, those of the isomer of the other skeletal series usually were, and the differences could be observed. The assignments of those compounds which were preivously unknown are given below.

4-Methyldibenzobicyclo[3.2.1.]octadiene, 13.

This compound has a mass spectral parent peak of 220, consistent with the structure, and a ratio of m/e of 178 to 205 of 0.30, indicative of the dibenzobicyclo-[3.2.1.] skeleton. Its glpc retention time was slightly longer than that of a synthesized sample of its isomer, 7-methyldibenzobicyclo[2.2.2.]octadiene, 19.

exo- and endo-4-tert-Butyldibenzobicyclo[3.2.1.]octadienes, 12 and 16.

The exo-isomer 12 was shown to be a tert-butyl coupling product by microanalysis and the endo-isomer 16 by mass measurement of the parent ion. When the physical and spectral properties of these compounds were compared to those of the dibenzobicyclo[2.2.2.] isomer 20, which had been synthesized by an unambiguous pro-

cedure, they were found to be different. Because there is no other alternative, these two compounds were assigned the [3.2.1.] structure. The ratio of m/e 178 to 205 of both 12 and 16 is less than unity whereas for the [2.2.2.] isomer 20 it is 83; these results support the [3.2.1.] skeleton assignment. The assignment of exo stereochemistry to isomer 12 is based upon nmr evidence. The coupling constant between endo-H_4 and H_5 is small (J = 1 Hz) and is consistent with the dihedral angle of ca. 80° between these atoms. There is precedent for such an assignment: $J_{4,5}$ for exo-4-chlorodibenzobicyclo-[3.2.1.]octadiene is 1.8 Hz (28) but for endo-4-chlorodibenzobicyclo[3.2.1.]octadiene $J_{4,5}$ is 5.0 Hz (38). If this assignment of exo stereochemistry is accepted, then the isomer 16, which was present in amounts too small to permit nmr analysis, must be, by elimination, the endo isomer.

exo- and endo-2-tert-Butoxydibenzobicyclo[3.2.1.]octadienes, 14 and 15.

In all, three tert-butoxy ethers were synthesized: the two isomeric [3.2.1.] ethers 14 and 15, and the [2.2.2.] ether 18. Since three different compounds were obtained when the corresponding alcohols were allowed to react with isobutylene, as was shown by their different melting points and nmr spectra, it would appear that there

was no change of stereochemistry during the syntheses and that each of the alcohols gave the corresponding ether. However, there is the possibility, albeit remote, that rearrangement through a carbonium ion could have taken place in one or more of the syntheses. Consequently, the skeletal type and stereochemistry of the three synthetic ethers had to be established.

All three compounds were shown by either microanalysis or parent peak mass measurement to have the requisite molecular formula. The presumed [2.2.2.] ether showed a ratio of m/e 178 to 205 of 29 which supports the assigned stereochemistry; the two presumed [3.2.1.] ethers both had a ratio of less than unity.

Nmr analysis served to confirm the assignments. The spectrum ($CDCl_3$) of the presumed [2.2.2.] ether 18 was similar to that of 7-phenylthiodibenzobicyclo[2.2.2.]-octadiene (28) especially in regard to the magnitude of the coupling constants, some of which are (value for ether 18 first, followed by value for phenylthio compound): $J_{1,7}$ = 3.0, 2.8; $J_{4,\underline{cis}\text{-}8}$ = 2.5, 2.6; $J_{\underline{trans}\text{-}7,8}$ = 3.25, 4.6; $J_{7,\underline{cis}\text{-}8}$ = 8.5, 9.2; $J_{\underline{cis}\text{-}8,\underline{trans}\text{-}8}$ = 12.5, 12.6 Hz. The spectra of the presumed exo-ether 14 and endo-ether 15 were very similar to one another, but with one important difference which allowed the assignment of exo and endo stereochemistry to be made: for the presumed exo isomer, $J_{1,\underline{endo}\text{-}2}$ = 2.2 Hz, and for the presumed

endo isomer, $J_{1,exo-2}$ = 8.5 Hz. Cristol (28) reports such differences in magnitudes for a large number of such exo and endo compounds.

Only two tert-butyl ethers were actually found during the analysis of the products of the decarbonylation reactions, and a comparison of their properties with those of the three synthesized ethers showed that the two reaction products were the exo and endo isomers and that the [2.2.2.] isomer was not produced.

bis-4-(Dibenzobicyclo[3.2.1.]octadiene), 17.

This dimer was not characterized fully. Mass spectral analysis gave a molecular ion at m/e 410. The ratio of m/e 178 to 205 was 0.10. A mass measurement was performed and the mass obtained (410.2036) agreed with that calculated (410.2035). Insufficient material was available to permit either an ir or nmr spectrum to be taken. The structural assignment of this compound must remain somewhat speculative.

It has been shown that 7-formyldibenzobicyclo-[2.2.2.]octadiene, 4, yields dibenzobicyclo[2.2.2.]octadiene and dibenzobicyclo[3.2.1.]octadiene only in the presence of a free-radical initiator. Further, when these hydrocarbons were heated in the presence of initiator, no reaction took place, indicating that the two hydrocarbons are thermally stable, even in the

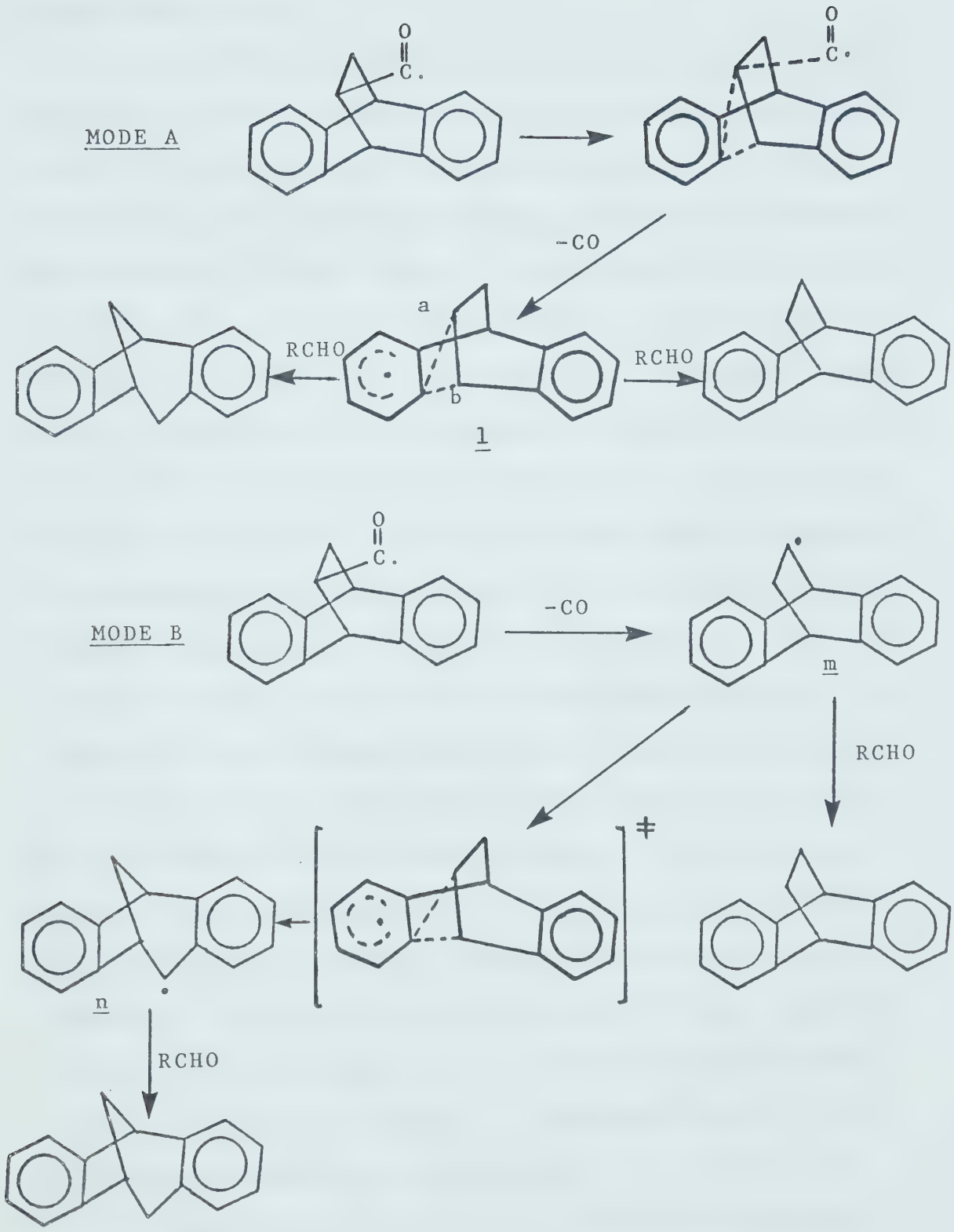
presence of initiator, under the conditions employed in the decarbonylation studies. Thus the formation of the isomeric hydrocarbons is a result of the free-radical decarbonylation of aldehyde 4 and they undergo no secondary reactions after their formation.

Having established that rearrangement did occur in this system, it was necessary to determine the nature of the intermediate involved in the rearrangement process. At least two different modes of radical rearrangement can be posited to explain the formation of the hydrocarbons 11 and 7 upon decarbonylation of aldehyde 4. (See Scheme III).

Both of these processes are intramolecular ones. They differ from one another in that Mode A contains an intermediate or energy minimum which is non-classical in type, whereas Mode B contains a transition state or energy maximum along the reaction path by which radical m rearranges to radical n.

There is much evidence in the literature that the neophyl rearrangement proceeds through two discrete radicals. (See pp. 5 to 7 of this thesis for a discussion of the arguments on this point). Usually it is assumed that the two radicals are the non-classical unrearranged and rearranged ones, although the non-classical radical could be one of the two radicals involved. However, if a bridged radical is formed, then the work of Ruechardt

SCHEME III



(16), Kochi (14) and Fischer (17) indicates that it is present only as a short-lived intermediate or as a transition state.

It should be possible to distinguish between the two postulated modes of reaction by carrying out the decarbonylation at differing initial concentrations of the aldehyde 4. This is the technique pioneered by Winstein and Seubold (7a) and has been used successfully by Tanner and Law (39). If Mode A is operating, the non-classical radical which is formed will represent an energy minimum along the path and will therefore be subjected to transfer at C_a and C_b to the same relative extent regardless of the concentration of the hydrogen atom donor (aldehyde 4). Thus the ratio of dibenzobicyclo[2.2.2.]octadiene, 11, and dibenzobicyclo[3.2.1.]octadiene, 7, should remain constant. In view of the formation of the coupling products in the reaction, this statement should be amplified to include attack by radicals produced from the initiator as well as by hydrogen transfer with radical 1. In contrast, Mode B requires a competition between hydrogen abstraction by radical m and rearrangement of this radical to radical n. Thus, by slowing the rate of chain transfer by reducing the concentration of the aldehyde hydrogen donor, it should be possible to increase the ratio of rearranged product to unrearranged.

As seen in Table I, both the ratios of dibenzobi-

cyclo[3.2.1.]octadiene to dibenzobicyclo[2.2.2.]octadiene, and of products with the [3.2.1.] skeleton to products with the [2.2.2.] skeleton do depend on the initial concentration of 7-formyldibenzobicyclo[2.2.2.]octadiene. A plot of initial concentrations of aldehyde 4 against the ratios of rearranged products to unrearranged products is shown in Figure IV. The lower the aldehyde concentration, the greater is the extent of rearrangement. Thus, Mode A cannot be operating in this reaction.

When 2-formyldibenzobicyclo[3.2.1.]octadiene, 5, is decarbonylated under the same conditions as was 7-formyldibenzobicyclo[2.2.2.]octadiene, 4, no rearrangement products are found (Table III). Perhaps this result is not too surprising, since rearrangement in this case would involve conversion of a secondary benzylic radical to a secondary aliphatic one. Slaugh (11) has shown that when the stability of the rearranged and unrearranged radicals is the same, then the extent of rearrangement is governed by the length of time available to the unrearranged radical before it disappears by transfer. In a situation where the rearranged radical is much more stable than the unrearranged one, it would be expected that the rearranged radical, once formed, would not return to the unrearranged form. It has been shown (7d,12) that the extent of rearrangement upon decarbonylation of aldehydes decreases on addition of a hydrogen donor, such as

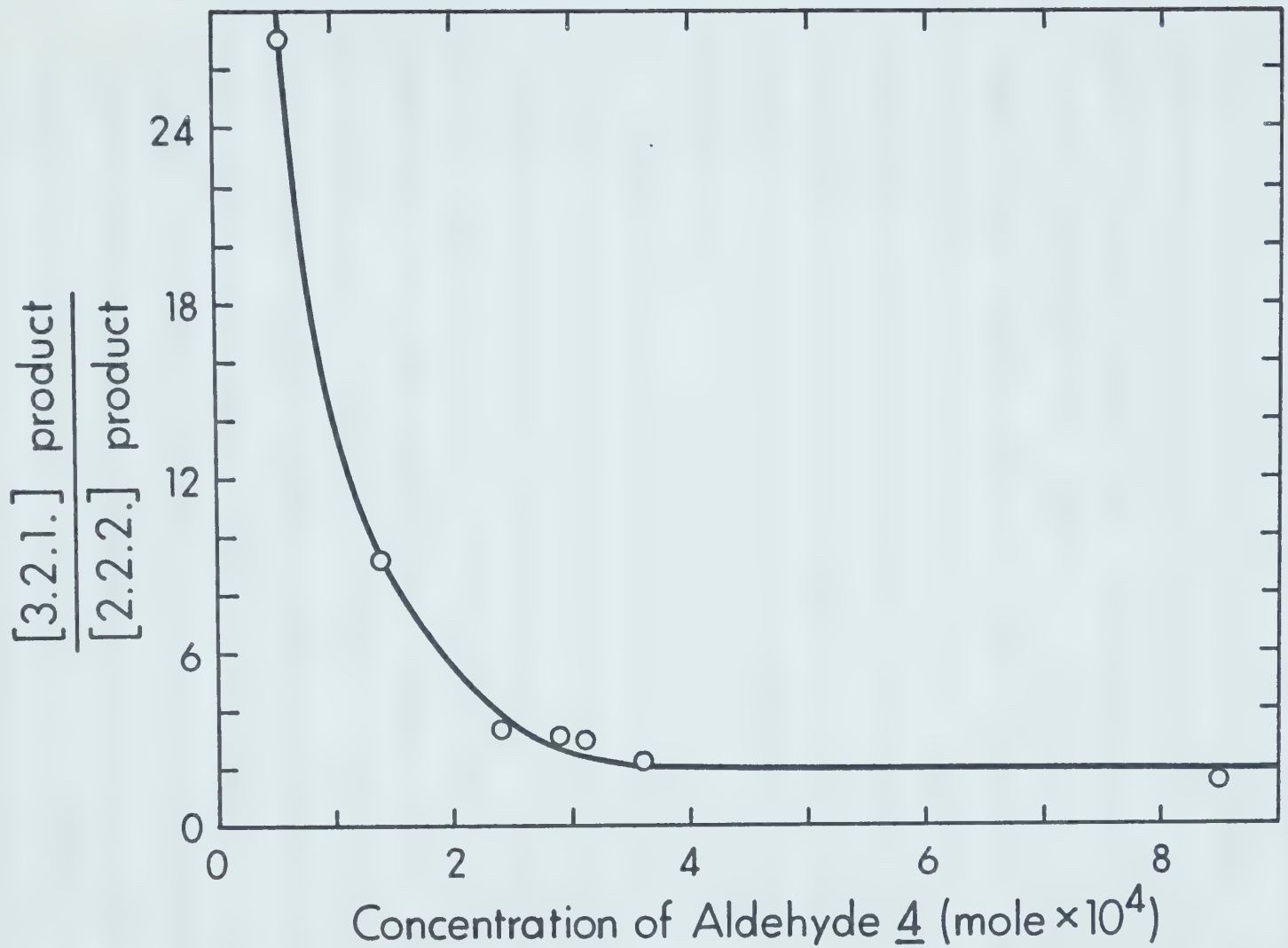


FIGURE IV Ratio of rearranged to unrearranged products from decarbonylation of 7-formyldibenzobicyclo[2.2.2.]octadiene at 84° vs initial aldehyde concentration.

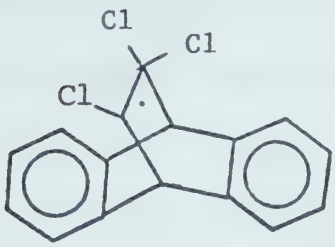
benzyl mercaptan or thiophenol. These results are in accord with those of the present study, where the hydrogen donor is the aldehyde itself, and it would appear, other things being equal, that the rearranged [3.2.1.] radical n has a longer lifetime than the unrearranged [2.2.2.] radical m because of the nature of the coupling products found in the reaction mixture. The fact that all such products contain the [3.2.1.] skeleton, despite the more sterically hindered environment for the coupling radical, indicates that the [3.2.1.] radical is the one with the longer lifetime, but yet shows no proclivity towards rearrangement.

There is the possibility that the reluctance of the [3.2.1.] radical to interconvert to the [2.2.2.] radical is due to a high energy of activation for the process. When the decarbonylation of 2-formyldibenzobicyclo[3.2.1.]-octadiene, 5, was performed at 120° instead of 84°, there was no dibenzobicyclo[2.2.2.]octadiene formed, nor were any of the attendant coupling products of that series. When 7-formyldibenzobicyclo[2.2.2.]octadiene, 4, was similarly decarbonylated at this higher temperature under optimum conditions for rearrangement (i.e. at low concentration), there was no increase in the amount of dibenzobicyclo[2.2.2.]octadiene produced; however, it must be pointed out that the material balance under these conditions was poor. It would appear that the [3.2.1.]

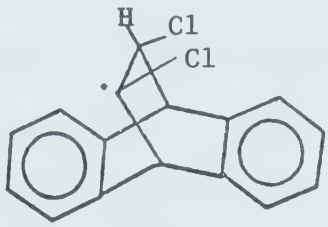
radical does not return to the [2.2.2.] radical because of its much greater stability. This stability can be attributed to its benzylic structure.

The results of this study should be contrasted with those of the study of Jarvis *et al.* (24,25). These workers found that the reduction of 7,7,8,8-tetrachlorodibenzobicyclo[2.2.2.]octadiene, 23, by tri-*n*-butyl tin hydride gave both 7,7,8-trichlorodibenzobicyclo[2.2.2.]-octadiene, 24, and the product of rearrangement 1,8,8-trichlorodibenzobicyclo[3.2.1.]octadiene, 25. Under 'dilute' conditions (0.00145 mole 23, 80 ml benzene, 0.00142 mole tri-*n*-butyl tin hydride) an nmr spectrum of the reaction mixture showed unrearranged trichloride 24 (32%), rearranged trichloride 25 (42%), 7,8-*trans*-dichlorodibenzobicyclo[2.2.2.]octadiene (15%) and unreacted starting material (10%). There was also a trace of 7,8-dichlorodibenzobicyclo[2.2.2.]octatriene product (*ca.* 1%). Under 'concentrated' conditions (0.00145 mole 23, 30 ml benzene, 0.0023 mole tri-*n*-butyl tin hydride) an nmr spectrum revealed no rearranged trichloride 25 but there was present unrearranged trichloride 24 (80%) and 7,8-*trans*-dichlorodibenzobicyclo[2.2.2.]octadiene (20%). When 7,7,8,-trichlorodibenzobicyclo[2.2.2.]octadiene was reacted with tri-*n*-butyl tin hydride under these conditions, no rearranged product was formed, even at high dilution. Jarvis ascribes the rearrangement of radical

q to steric inhibition to chain transfer caused by the presence of two β-chlorine atoms, whereas with radical r there is only one β-chlorine present. This would appear to be a situation where the lifetime of the radical is important and it would be interesting to study whether the [3.2.1.] radical s, initially generated, would rearrange to the [2.2.2.] radical, since the pronounced



q



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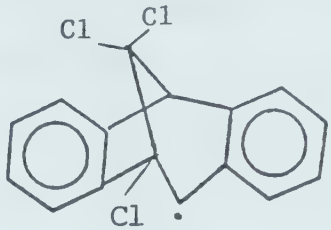
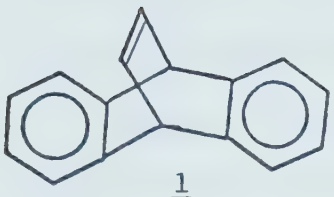


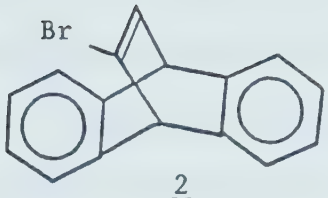
s

steric crowding of the [3.2.1.] radical would ensure it a long lifetime.

These workers also found rearrangement product when olefins 1, 2, and 3 were allowed to react with carbon tetrahalides (25). They noted that the tendency towards rearrangement in these reactions increases with a) increasing temperature, b) decreasing concentration of chain-transfer reagent (Cl_3CSO_2Cl or Cl_3CBr), c) on changing from Cl_3CBr to Cl_3CSO_2Cl and d) on changing from olefin 1 to the vinyl halides 2 and 3. The first two trends have been noted in this present study and the other two can be rationalized on the basis that the



1



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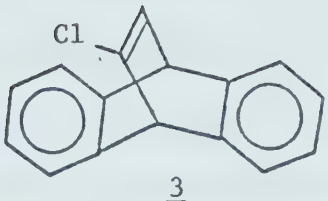

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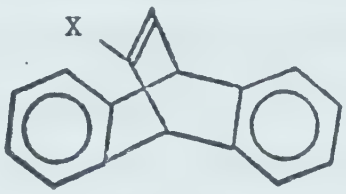
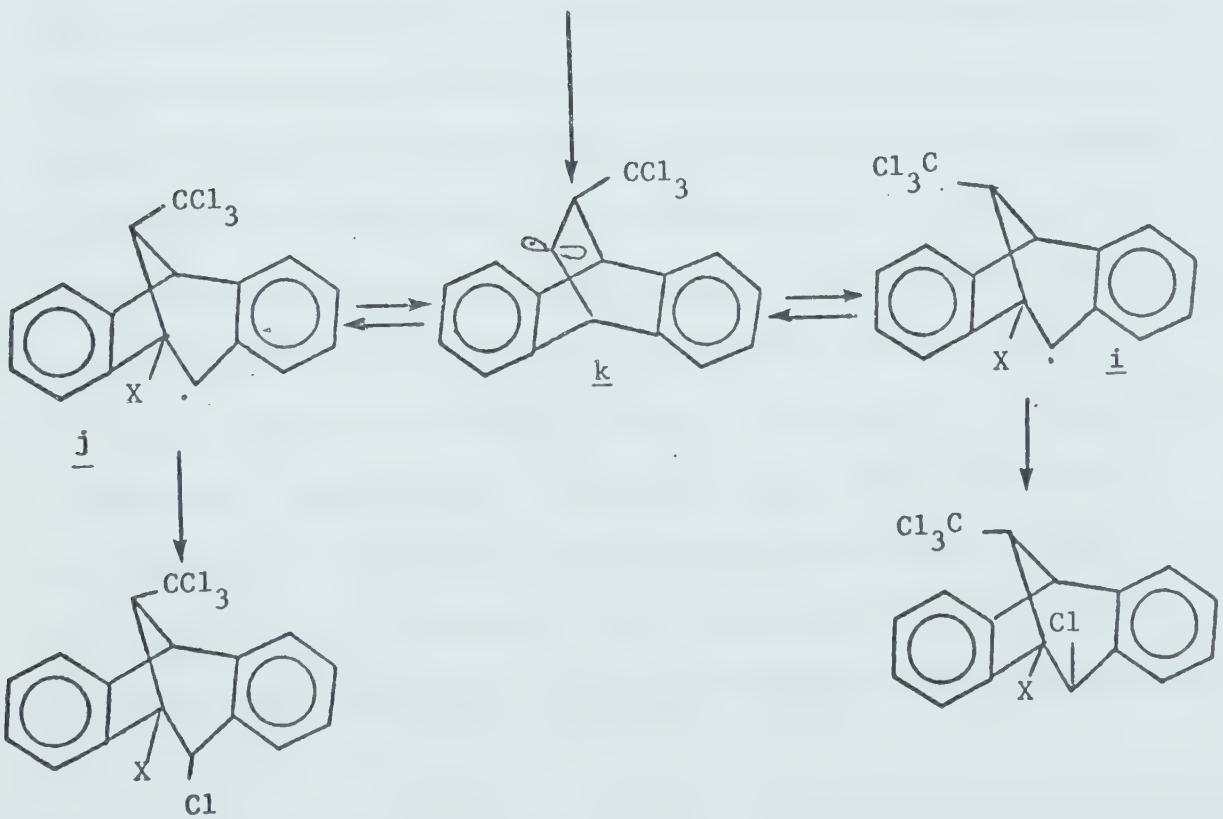
changes involved increase the lifetime of radical k. Thus, the positioning of a halide atom β to the radical center should stabilize the radical and further, should sterically hinder chain transfer. Jarvis suggests that



1, X = H
2, X = Br
3, X = Cl



Cl_3CSO_2Cl is not as good a chain transfer agent as is Cl_3CBr and so this explains the third tendency above.

Jarvis also found that the rearranged radicals were formed reversibly because the product from i gained more than that from j when a) the temperature was raised, b) the concentration of chain-transfer agent was lowered, c) the chain-transfer reagent was changed from Cl_3CBr to Cl_3CSO_2Cl and d) the vinyl halides were the substrates. The radical j gives only endo substitution whereas radical i tends to give exo product. In the case of radical j, the more favoured exo attack is blocked by the substituent at C-8 and so it has a longer lifetime than if the substituents were not there. It then rearranges to the [2.2.2.] radical k which in turn rearranges to the anti-8-substituted radical i. Because the substituent is now not blocking exo attack, this radical transfers more readily and so the concentration of the resultant product increases. No such effect was observed in the course of this present study. It would appear that although the dibenzobicyclo[3.2.1.]octadienyl radical has a longer lifetime compared to its [2.2.2.] counterpart, it does not rearrange. Presumably, the reason for this result can be given as being due to the greater stability of the benzylic [3.2.1.] radical over the alkyl [2.2.2.] radical and that coupling, almost exclusively from exo attack,

takes place before the radical has a chance to return to the [2.2.2.] system. Alternatively, it is possible that the results of Jarvis arise from the presence of two σ radicals, as was discussed in the introduction, in which case there would be no need to invoke a rearrangement of a [3.2.1.] radical to a [2.2.2.] radical and hence the results of this study and that of Jarvis would be in accord. However, the [3.2.1.] radical may indeed rearrange to the [2.2.2.] radical in Jarvis's system, because the stability of the α-bromo-[2.2.2.] radical may be closer in stability to the [3.2.1.] benzylic one.

EXPERIMENTAL

I. MATERIALS AND REAGENTS

Solvents. Dichloromethane was washed with concentrated sulfuric acid, saturated sodium chloride solution and water, dried over calcium chloride and distilled. It was stored over molecular sieve, 4A. Dioxane was passed through a chromatography column (80 g of activated alumina for 100 ml of dioxane) to remove peroxides, and was then purified according to the method of Fieser (40). Diethylene glycol dimethyl ether (diglyme) was obtained from Matheson Coleman and Bell Co. Ltd. and was heated to reflux over sodium metal for several hours and then distilled from the sodium. Tetrahydrofuran (THF) was distilled from lithium aluminum hydride and used immediately. Dimethylsulfoxide (DMSO) was stored over calcium hydride and was distilled from the storage flask as required. Chlorobenzene was washed with concentrated sulfuric acid and then water, dried over anhydrous sodium sulfate, then distilled from sodium.

Reagents. Blue-violet fluorescent anthracene was obtained from Aldrich Chemical Company and was used without further purification. Biphenyl was recrystallized from carbon tetrachloride and n-pentane; it melted at 70-71° and was shown to be pure by glpc analysis. Boron trifluoride etherate was obtained from Eastman Kodak Co.

and was distilled prior to use. Acrolein was obtained from Terochem Laboratories Ltd. and was distilled into a flask containing a trace of hydroquinone. 3,3-Dimethylbutene was obtained from Aldrich Chemical Co. and was distilled before use. Chromium trioxide was stored over phosphorus pentoxide in a vacuum desiccator for at least twenty-four hours before use. Pyridine was distilled from barium oxide and was stored over molecular sieve, 4A. tert-Butanol was distilled from sodium. Ethyl chloroacetate was distilled using a Vigreux column; after a considerable forerun of low-boiling contaminants, the pure compound was collected at 142° (714 Torr). n-Butyl lithium was supplied by Foote Chemicals as a solution (1.5 M in n-hexane).

trans-7,8-Dichlorodibenzobicyclo[2.2.2.]octadiene was made by the reaction of anthracene and trans-1,2-dichloroethylene according to the method of Cristol (30). Physical properties (30) and spectra (29) were identical to those reported. Dibenzobicyclo[2.2.2.]octatriene, 1, was prepared by the method of Cristol (27). The physical properties (27) and nmr spectrum (29) were identical to those reported. syn-8-Iododibenzobicyclo[3.2.1.]octadien-2-yl acetate was made by the method of Cristol (27) as modified by Lutzer (38) using the Prevost reaction of silver acetate on dibenzobicyclo[2.2.2.]octatriene, 1. Physical properties and nmr spectra were identical to

those reported (38). Dibenzobicyclo[3.2.1.]octadien-2-yl acetate, 27, was prepared by the Raney nickel and hydrogen reduction of syn-8-iododibenzobicyclo[3.2.1.]octadien-2-yl acetate according to the procedure of Lutzer (38). Physical properties and nmr spectrum were identical to those reported (38). The acetate 27 was reduced with lithium aluminium hydride according to the method of Cristol (41). The spectral properties of the mixture of exo- and endo-dibenzobicyclo[3.2.1.]octadien-2-ols, 28, were identical to those reported (28). Dibenzobicyclo-[2.2.2.]octadiene, 11, was made by the reduction of dibenzobicyclo[2.2.2.]octatriene, 1, using hydrogen at one atmosphere with a platinum oxide catalyst, following the method of Cristol and Hause (30). Its physical properties (30) and nmr spectrum (29) were identical to those reported. Trimethylsulfonium iodide was made by the reaction of methyl iodide and dimethylsulfide according to the method of Corey and Chaykovsky (33).

II. PREPARATION OF SUBSTRATES AND AUTHENTIC SAMPLES

7-Formyldibenzobicyclo[2.2.2.]octadiene, 4 ,- The aldehyde was prepared after the manner of Murahashi et al. (26). In each of a series of Carius tubes was placed anthracene (10 g, 0.0575 mole), distilled acrolein (4 ml, 3.36 g, 0.06 mole) and benzene (15 ml). The

tubes were sealed and then heated at 140° for 12 hours. The reaction mixtures from four such tubes were concentrated by rotary evaporation and the residual syrup was dissolved in methanol (250 ml). The unreacted anthracene was removed by filtration. An equal volume of ice-cold water was added slowly and with shaking to the methanolic solution. When a solid began to appear, the mixture was left to stand overnight at 0°. The solid was filtered off and the cake of crude aldehyde monohydrate was dried in the vacuum oven at 50° overnight. The residue was dissolved in carbon tetrachloride and boiled with activated carbon. The solution was filtered and the solvent was removed by rotary evaporation. The aldehyde was recrystallized several times from carbon tetrachloride and 60 - 90° ligroine to yield 16.3 g (0.70 mole, 30.2%): mp 95 - 96° (lit. 95° (26)); ir (CCl_4) cm^{-1}: 3025 m, 2590 m, 2710 w, 1725 s, 1455 s, 1130 m, 878 m; nmr ($CDCl_3$): τ 0.6 (doublet, 1H, C<u>H</u>O), 2.60 - 3.20 (multiplet, 8H, aromatic), 5.32 (doublet, 1H, H_1, $J_{1,7}$ = 2.5 Hz), 5.68 (triplet, 1H, H_4, $J_{4,\underline{cis}\text{-}8} \simeq J_{4,\underline{trans}\text{-}8}$ = 2.6 Hz), 7.14 (multiplet, 1H, H_7), 7.96 (multiplet, 2H, <u>cis</u>-H_8 and <u>trans</u>-H_8); mass spectrum (115°, E.I.) m/e (relative intensity > 5%): 234 (M, 6.4), 179 (27), 178 (100), 176 (7.2), 88 (5.8), weak but structurally significant peak at 205 (1.5).

The semicarbazone derivative was made according to

the procedure of Vogel (42) to yield white crystals: mp 199.5 - 200°.

Anal. Calcd for $C_{18}H_{17}N_3O$: C, 74.20; H, 5.88; N, 14.42. Found: C, 74.50; H, 6.08; N, 14.65.

Dibenzobicyclo[3.2.1.]octadien-2-one, 8 ,- The method of oxidation of the alcohols 28 which was chosen was that of chromium trioxide and pyridine in dichloromethane, using a procedure modified from that of Ratcliffe and Rodehorst (43). Chromium trioxide (6.0 g, 0.06 mole) was added to a magnetically stirred solution of pyridine (9.49 g, 0.12 mole) in dichloromethane (150 ml) contained in a 500-ml flask. The flask was stoppered with a drying tube and the initially yellow, then plum red, solution was stirred for 15 minutes at room temperature. Then a solution of the alcohol 28 (2.22 g, 0.01 mole), dissolved in a small volume of dichloromethane, was added to the oxidation medium in one portion. A tarry, black deposit separated immediately. After being stirred for an additional 15 minutes at room temperature, the solution was decanted from the residue and the residue was washed with ether (200 ml). The organic solutions were combined and washed with 5% aqueous sodium hydroxide (3 x 100 ml), 5% hydrochloric acid (100 ml), 5% aqueous sodium bicarbonate (100 ml) and saturated sodium chloride solution (100 ml). The organic layer was dried over anhydrous

sodium sulfate. After filtration of the drying agent, the solvents were removed by rotary evaporation to yield the crude ketone. This material was dissolved in the minimum amount of 50:50/Skelly B:carbon tetrachloride and placed on a chromatography column (acid-washed alumina, 10 g). Elution with 75:25/carbon tetrachloride: chloroform gave the ketone. Some residual alcohol was eluted with neat chloroform. The ketone fractions were combined and the solvents removed by rotary evaporation to yield 1.95 g (0.0075 mole, 75%). The ketone was recrystallized twice from 98% ethanol to give white needles: mp 106 - 107° (lit. 115° (27)). The nmr spectrum was identical to that reported (28); the infrared spectrum showed a strong absorption at 1700 cm^{-1}.

2-Formyldibenzobicyclo[3.2.1.]octadiene, 5, by the Darzens Glycidic Ester Condensation - The method of Hunt, Chinn and Johnson was modified (44). Clean potassium (0.18 g, 0.0046 mole) was allowed to react with dry tert-butanol (3.7 ml). The condensation was conducted in a 50-ml round-bottomed three-necked flask containing a magnetic stirring bar and to which was fitted a thermometer and a pressure-equalizing dropping funnel. The top of the funnel was connected to a system for exhausting and filling with nitrogen. The whole apparatus was dried and then was added to the flask ethyl chloro-

acetate (0.5 ml, 0.558 g, 0.0046 mole), dibenzobicyclo-[3.2.1.]octadien-2-one, 8 (1 g, 0.0046 mole) and enough tert-butanol to effect solution (ca. 6 ml). To avoid the solidification of the alcohol solvent, a co-solvent of carbon tetrachloride was added (6 ml). The solution of potassium tert-butoxide (0.0046 mole) in tert-butanol was introduced to the dropping funnel and the system was flushed with nitrogen three times. The flask was cooled in an ice-bath, stirring was started, and the solution of tert-butoxide was added so as to keep the temperature between 10 - 15°. The addition took 10 minutes. The mixture was stirred for a further hour at 15°. tert-Butanol was removed by rotary evaporation and the residue, a brown oil, was dissolved in ether. The ether solution was washed with water, saturated sodium chloride solution and then dried over anhydrous sodium sulfate. After the filtration of the drying agent, the solvent was removed by rotary evaporation to leave a pale yellow oil (1.1 g). The crude glycidic ester was used in the subsequent stage. Ir (CCl_4) cm^{-1}: 1700 s, unreacted ketone, 1200 m, epoxide ring breathing.

The ester was hydrolyzed and decarboxylated according to a modified method of Allen and VanAllan (45). The crude 1'-oxaspiro[2.6.]-2-dibenzobicyclo[3.2.1.]octadiene-2'-carboxylic acid, ethyl ester was added to a 50 ml round-bottomed flask fitted with a reflux condenser

and containing sodium (0.10 g, 0.0043 mole) in ethanol (2 ml). Water (0.15 ml) was added, whereupon the sodium salt precipitated as a brown solid. The mixture was allowed to stand overnight and the brown precipitate was filtered and then triturated with carbon tetrachloride. The slurry was filtered and washed with ethanol (2 ml) and carbon tetrachloride (6 ml). The solid was dried under reduced pressure at 60° for twelve hours.

In a 100-ml round-bottomed flask fitted with a reflux condenser were mixed water (4 ml) and concentrated hydrochloric acid (0.7 ml), and to this solution was added the powdered, dried salt. The mixture started to froth, showing the evolution of carbon dioxide. The flask was heated on a steam bath for 1.5 hours whereupon the aldehyde formed an oil on the surface of the acid. The flask was cooled and its contents extracted with benzene (20 ml). The extract was washed with water and dried over anhydrous sodium sulfate. After filtration of the drying agent, the solvent was removed by rotary evaporation to yield an oil (0.185 g). The infrared spectrum of this oil showed carbonyl absorptions at 1720 cm^{-1} and 1700 cm^{-1} indicating the presence of both aldehyde and unreacted ketone. There was also present an aldehyde C-H stretch absorption at 2715 cm^{-1}. Glpc analysis of the oil (4 ft x 0.25 in NPGS) showed that the ratio of aldehyde to ketone was 60/40, and so the

yield of aldehyde was 0.105 g (10%).

In an attempt to improve the yield of aldehyde, sodium ethoxide in ethanol was used as the base. The procedure was the same as has been described above. Ethyl chloroacetate was used in excess as the co-solvent. In the flask were placed ethyl chloroacetate (5 ml, 5.58 g, 0.046 mole), ketone 8 (1.8 g, 0.008 mole) and ethanol (3 ml). To this was added the product of the reaction of sodium (0.3 g, 0.013 mole) and ethanol (3 ml). The subsequent hydrolysis and decarboxylation were repeated as described above. There was no aldehyde produced; the ketone was recovered (1.6 g, 0.0072 mole). The Darzens condensation was repeated using once again potassium tert-butoxide in tert-butanol as the base system, but at a higher temperature (28°). No aldehyde was produced.

2-Formyldibenzobicyclo[3.2.1.]octadiene, 5, by Reaction with Dimethylsulfoniummethylide - The method of Corey and Chaykovsky (33) was extensively modified to yield 1'-oxaspiro[2.6.]-2-dibenzobicyclo[3.2.1.]octadiene and the epoxide was then opened to give the required aldehyde. The apparatus consisted of a 300-ml three-necked flask fitted with a nitrogen inlet and a drying tube. The center neck was fitted with a jacketed pressure-equalizing dropping funnel which had the normal neck and also a further port alongside the usual one. This

port was covered with a serum stopper and a mechanical stirrer was fitted to the neck through an air-tight sleeve. The jacket was filled with carbon tetrachloride and kept at a temperature of -5° by the judicious addition of Dry Ice. The dropping funnel was charged with a solution of trimethylsulfonium iodide (2.53 g, 0.012 mole) in dry dimethylsulfoxide (DMSO) (55 ml) and dry tetrahydrofuran (THF) (45 ml). In the reaction flask was placed a magnetic stirring bar and a solution of dibenzobicyclo[3.2.1.]octadien-2-one (1.76 g, 0.008 mole) in dry THF (50 ml) and the flask was kept at -25° with Dry Ice and carbon tetrachloride. The whole system was then alternately evacuated and filled with dry nitrogen three times. Using a pre-cooled syringe, n-butyl lithium (8.0 ml of 1.5 M solution in hexane, 0.012 mole) was added to the dropping funnel over a period of twenty minutes with constant stirring. The ylide was then added with continued mechanical stirring to the solution of the ketone which was magnetically stirred. The addition took 1 hour. The reaction mixture was stirred for an additional 15 minutes at -25° and was then allowed to warm to room temperature with the stirring being continued. The reaction was quenched by the addition of water (200 ml) and was extracted with ether (2 x 100 ml). The organic layer was washed with water (10 x) to remove THF and DMSO and was dried with

anhydrous sodium sulfate. After filtration of the drying agent, the solvents were removed by rotary evaporation to yield an oil (2.05 g); ir (CCl_4) cm^{-1}: 1700 (unreacted ketone), 1255 (epoxide (46)).

The crude material was used in the next stage without further purification, as previous work had shown that the epoxide was prone to ring opening to give an alcohol. The residual oil was dissolved in ether (60 ml) and to this solution was added, with stirring, boron trifluoride etherate (10 ml, 11.58 g, 0.084 mole). The flask was fitted with a drying tube and the mixture was stirred at room temperature for 30 minutes. Water was added with caution to destroy the residual etherate. In a separatory funnel the water was removed. To the organic layer was added aqueous saturated sodium bicarbonate until all effervescence ceased. The organic layer was dried overnight over anhydrous sodium sulfate. After filtration of the drying agent, the solvent was removed by rotary evaporation to yield an oil (2.0 g). Separation of the aldehydes from unreacted ketone was partially achieved by the dry-column technique (see below). Spectral analysis was performed on a sample collected by glpc (2 ft x 0.25 in NPGS) which was free of ketone 8.
Ir (CCl_4) cm^{-1}: 3080 m, 3015 m, 2950 s, 2880 m, 2710 w, 1725 s, 1485 m, 1470 m, 1455 m, 1170 s; nmr ($CDCl_3$) one isomer: τ 0.10 (doublet, 1H, -C<u>H</u>O, $J_{C\underline{H}O,H_4}$ = 2.0

Hz), 2.80 - 3.20 (multiplet, 8H, aromatic), 6.09 (multiplet, 1H, H_1), 6.21 (multiplet, 1H, H_5), 6.52 (multiplet, 1H, H_4), 7.50 (multiplet, 1H, anti-H_8), 7.88 (multiplet, 1H, syn-H_8); other isomer: τ 0.68 (doublet, 1H, -CHO, J_{CHO,H_4} = 3.0 Hz), 2.80 - 3.20 (multiplet, 8H, aromatic), 6.09 (multiplet, 1H, H_1) 6.21 (multiplet, 1H, H_5), 6.62 (multiplet, 1H, H_4), 7.50 (multiplet, 1H, anti-H_8), 7.88 (multiplet, 1H, syn-H_8); mass spectrum (150°, E.I.), m/e (relative intensity > 20%): 234 (M,27), 206 (30), 205 (100), 204 (23), 203 (27), 202 (21), 178 (25).

Mass Measurement: Calcd for $C_{17}H_{14}O$: 234.1045. Found: 234.1039.

The semicarbazone derivative was made according to the procedure of Vogel (42) and was recrystallized twice from ethanol; mp: 214 - 216.5°.

Anal. Calcd for $C_{18}H_{17}N_3O$: C, 74.20; H, 5.88; N, 14.42. Found: C, 74.04; H, 5.97; N, 14.55.

Chromatographic Separation of 2-Formyldibenzobicyclo[3.2.1.]octadiene and Dibenzobicyclo[3.2.1.]octadiene-2-one -

(a) The most successful column technique proved to be one where a nylon column was used; aldehyde and ketone mixture (2.1 g) was dissolved in dichloromethane (10 ml) and placed on a silica gel column (Woelm Silica for Dry Columns, 50 g, treated with an electronic

phosphor). The column was developed with dichloromethane until the solvent front reached the base of the column. The bands of aldehyde and ketone were observed under ultraviolet light and this section of the column was cut into four sections. The silica gel of each of these cuts was extracted with ether, the ether was dried over anhydrous sodium sulfate and, after filtration of the drying agent, the solvent was removed by rotary evaporation. The lowest two sections yielded a colorless oil (0.605 g) which was shown by thin-layer chromatography to be almost only aldehyde, and which was shown by glpc (see below) to contain 90% aldehyde and 10% ketone and no other compounds. Thus the yield of aldehyde was 0.548 g (0.0023 mole, 38%).

(b) Gas-liquid Partition Chromatography (glpc). Whilst several liquid phases were found to be able to separate the ketone and the aldehyde, the one chosen was neopentyl glycol succinate (NPGS). A 4 ft x 0.25 in glass column was packed with 10% NPGS on Chromasorb P, A/W and was able, with a carrier gas flow of 100 ml per minute to separate the aldehyde from the ketone at 150°. In this way it was found that the colorless oil isolated by the nylon column technique was 90% aldehyde and 10% ketone.

7-*tert*-Butoxydibenzobicyclo[2.2.2.]octadiene, 18 , -

The method of Beyerman and Bonjekoe (47) for the synthesis of *tert*-butyl ethers was followed with modifications. Dibenzobicyclo[2.2.2.]octadien-7-ol (0.6 g, 0.0027 mole) (38) was dissolved in dichloromethane (25 ml) and poured into a 2 l. pressure vessel equipped with a magnetic stirring bar. To this was added Dowex 50W - X8 Strongly Acidic resin (2 g). Isobutylene was condensed by passing the gas into a flask cooled by Dry Ice. The liquefied isobutylene (21 ml, 11.88 g, 0.21 mole) was poured into the pressure vessel and the vessel was sealed. The contents were stirred overnight at room temperature. The pressure was released and the resin was filtered off and washed with dichloromethane (20 ml). The dichloromethane of the filtrate and washings was removed by rotary evaporation to yield a white solid (0.58 g). The crude material was dissolved in a small amount (10 ml) of 70:30/carbon tetrachloride:pentane and was placed on a dry column (acid-washed alumina, 18 g). The required ether was eluted with more of the same solvent. The first four fractions of 100 ml contained a total of 0.325 g of the ether (0.0012 mole, 43%). The ether was recrystallized from carbon tetrachloride and pentane: mp 144.5 - 145°; ir (CCl_4) cm^{-1}: 3080 w, 3050 w, 3030 m, 2980 s, 2920 m, 1470 m, 1460 m, 1390 m, 1370 w, 1365 m, 1215 s, 1195 s, 1180 w, 1170 w, 1145 w, 1115 w, 1095 w,

1060 s, 1025 m, 995 m, 920 w, 870 w, 665 s, 630 w, 610 w; nmr (CCl_4): τ 2.70 - 3.20 (multiplet, 8H, aromatic), 5.90 (triplet, 1H, H_4, $J_{4,8}$ = 2.6 Hz), 5.92 (doublet, 1H, H_1, $J_{1,7}$ = 3.0 Hz), 6.11 (doublet of doublet of doublet, 1H, H_7, $J_{7,\underline{trans}\text{-}8}$ = 8.5 Hz, $J_{7,\underline{cis}\text{-}8}$ = 3.25 Hz, $J_{7,1}$ = 3.0 Hz), 7.88 (doublet of doublet of doublet, 1H, $H_{\underline{trans}\text{-}8}$, $J_{\underline{trans}\text{-}8,\underline{cis}\text{-}8}$ = 12.5 Hz, $J_{\underline{trans}\text{-}8,7}$ = 8.5 Hz, $J_{\underline{trans}\text{-}8,4}$ = 2.6 Hz), 8.64 (doublet of doublet of doublet, 1H, $H_{\underline{cis}\text{-}8}$, $J_{\underline{cis}\text{-}8,\underline{trans}\text{-}8}$ = 12.5 Hz, $J_{\underline{cis}\text{-}8,7}$ = 3.25 Hz, $J_{\underline{cis}\text{-}8,4}$ = 2.6 Hz), 8.91 (singlet, 9H, tert-butyl); mass spectrum (115°, E.I.) m/e (relative intensity > 3.5%): 221 (3.8), 205 (3.5), 203 (6.1), 179 (22), 178 (100); mass spectrum (50°, NH_3-C.I.) m/e (relative intensity > 10%): 296 (M + 18, 100).

Anal. Calcd for $C_{20}H_{22}O$: C, 86.28; H, 7.97. Found: C, 86.00; H, 7.95.

exo-2-tert-Butoxydibenzobicyclo[3.2.1.]octadiene, 14,- The procedure detailed for the synthesis of 7-tert-butoxydibenzobicyclo[2.2.2.]octadiene was followed exactly. Dibenzobicyclo[3.2.1.]octadien-exo-2-ol (0.81 g, 0.0037 mole) was reacted with isobutylene (20 ml, 11.88 g, 0.21 mole) to yield, after chromatography, a white solid (0.59 g) which was shown by glpc analysis (4 ft x 0.25 in NPGS) to consist of two compounds in the ratio of 1:3. The lesser component gave an nmr

spectrum consistent with 4-(2-methylpropenyl)dibenzobicyclo[3.2.1.]octadiene and the major component was the required ether in 43% yield. Mp 102.5 - 104°; ir (CCl_4) cm^{-1}: 3090 w, 3040 w, 2990 s, 2960 m, 2890 w, 1490 w, 1475 m, 1460 m, 1392 m, 1372 m, 1368 m, 1340 w, 1305 w, 1250 w, 1230 w, 1194 s, 1160 w, 1054 s, 1045 m, 1020 s, 945 w, 938 w, 920 w, 910 w, 600 w; nmr ($CDCl_3$): τ 2.60 - 3.20 (multiplet, 8H, aromatic), 5.56 (doublet, 1H, endo-H_2, $J_{2,1}$ = 2.2 Hz), 6.14 (broad triplet, 1H, H_5, $J_{5,anti\text{-}8} = J_{5,syn\text{-}8}$ = 2.7 Hz), 6.54 (multiplet, 1H, H_1), 7.58 (multiplet, 2H, syn-H_8 and anti-H_8), and 8.58 (singlet, 9H, tert-butyl); mass spectrum (80°, E.I.) m/e (relative intensity > 10%): 277 (M - 1, 25), 222 (34), 221 (38), 205 (48), 204 (100), 203 (36), 178 (19), weak but structurally important peak at 278 (M, 5).

Anal. Calcd for $C_{20}H_{22}O$: C, 86.28; H, 7.97. Found: C, 86.44; H, 8.08.

endo-2-tert-Butoxydibenzobicyclo[3.2.1.]octadiene, 15.- When the procedure detailed for the synthesis of the ethers 18 and 14 was followed, none of the required endo ether was obtained. Under more forcing conditions, a small amount of the ether was finally realized. Dibenzobicyclo[3.2.1.]octadien-endo-2-ol (0.51 g, 0.0023 mole) was dissolved in dichloromethane (25 ml) in a

pressure vessel fitted with a magnetic stirring bar. Then was added, in quick succession, condensed isobutylene (50 ml, 29.7 g, 0.52 mole) and concentrated sulfuric acid (1 drop). The vessel was sealed and the mixture was stirred for 2 days at room temperature. After chromatography, using the same conditions as before, a white solid was obtained in the first 100-ml fraction (0.005 g). There was no solid in subsequent fractions until the eluting solvent was changed to chloroform, whereupon unreacted alcohol (0.4 g) was recovered. Glpc analysis of the first fraction showed that the ether had formed but was contaminated by what appeared to be polymers of isobutylene. The required ether was collected by preparative glpc (2 ft x 0.25 in NPGS) to yield a white solid: mp 97 - 99.5°; yield <1%; nmr ($CDCl_3$): τ 2.60 - 3.20 (multiplet, 8H, aromatic), 5.10 (doublet, 1H, exo-H_2, $J_{2,1}$ = 8.5 Hz), 6.14 (multiplet, 1H, H_5), 6.50 (multiplet, 1H, H_1), 7.54 (multiplet, 2H, syn-H_8 and anti-H_8) and 8.48 (singlet, 9H, tert-butyl).

Mass Measurement. Calcd for $C_{20}H_{22}O$: 278.1671. Found: 278.1674.

7-Methyldibenzobicyclo[2.2.2.]octadiene, 19 , - The Clemmensen reduction of the aldehyde 4 was employed in this transformation. The aldehyde 4 (0.5 g, 0.0021 mole) was dissolved in 98% ethanol (10 ml). Zinc amalgam (3 g) was prepared by the method of Vogel (48). In a 100-ml

flask were placed the amalgam, the ethanolic solution of the aldehyde and concentrated hydrochloric acid (15 ml). The mixture was heated under reflux for 36 hours, then cooled and extracted with ether (31 ml in three extractions). The ethereal solution was washed with saturated sodium bicarbonate solution, saturated sodium chloride solution and then dried over anhydrous sodium sulfate. After the drying agent was filtered, the solvent was removed by rotary evaporation to yield a yellow oil (0.33 g, 0.0015 mole). The oil was taken up in the minimum amount of 70:30/pentane:carbon tetrachloride and this solution was placed on a dry column (Woelm Neutral Alumina, 7 g). The hydrocarbon was eluted with more of the same solvent. The first fraction yielded white cyrstals (0.29 g, 0.0013 mole, 63%); the second fraction contained no further product. A portion of the material was recrystallized from ice-cold pentane to give chunky crystals: mp 91 - 92° (lit. 89 - 92° (37)). The infrared spectrum was in accord with that reported (37). Nmr ($CDCl_3$): τ 2.60 - 3.20 (multiplet, 8H, aromatic), 5.80 (triplet, 1H, H_4, $J_{4,\underline{cis}\text{-}8} \simeq J_{4,\underline{trans}\text{-}8} = 2.2$ Hz), 6.06 (doublet, 1H, H_1, $J_{1,7} = 1.8$ Hz), 8.00 (multiplet, 2H, H_7 and $H_{\underline{trans}\text{-}8}$), 8.96 (doublet of doublets, 1H, $H_{\underline{cis}\text{-}8}$, $J_{\underline{cis}\text{-}8,\underline{trans}\text{-}8} = 7.5$ Hz, $J_{\underline{cis}\text{-}8,4} = 2.2$ Hz), 9.26 (doublet, 3H, methyl); mass spectrum (70°, E.I.) m/e (relative intensity > 5%): 220 (M, 6), 179 (16),

178 (100), weak but structurally important peak at 205 (1.5).

Anal. Calcd for $C_{17}H_{16}$: C, 92.68; H, 7.32. Found: C, 92.97; H, 7.11.

7-tert-Butyldibenzobicyclo[2.2.2.]octadiene, 20 , - In each of two Carius tubes was placed anthracene (10 g, 0.0575 mole), distilled 3,3-dimethylbutene (8 g, 0.095 mole) and toluene (15 ml). The tubes were sealed and then heated at 195° for 72 hours. After being cooled and opened, the tubes were emptied into a 500-ml flask and crushed maleic anhydride (25 g, 0.26 mole) with toluene (30 ml) was added. The contents of the flask were heated under reflux for 4 hours in order to remove the unreacted anthracene as the maleic anhydride adduct. The solution was cooled and extracted with a total of 2 l. of saturated sodium bicarbonate solution. The organic layer was washed twice with saturated sodium chloride solution and then dried over anhydrous sodium sulfate. After filtration of the drying agent, the solvent was completely removed by rotary evaporation and the brown residue was dissolved in 90:10/pentane:carbon tetrachloride (50 ml). The solution was placed on a dry column (acid-washed alumina, 200 g) and the hydrocarbon was eluted with 90:10/pentane:carbon tetrachloride. The first four fractions of 100 ml contained 0.125 g, 1.12 g, 1.45 g and

0.025 g, respectively, of material. Nmr analysis showed the first and the last fraction to be identical so all the fractions were combined (1.72 g, 0.0059 mole, 5.15%, based on anthracene). The hydrocarbon was recrystallized from pentane: mp 76 - 76.5°; ir (CCl_4) cm^{-1}: 3080 w, 3050 w, 3030 m, 2970 s, 2910 m, 2880 m, 1485 w, 1470 s, 1460 m, 1395 w, 1365 m, 1290 w, 1210 w, 1190 w, 1170 w, 1142 w, 1115 w, 1050 w, 1025 w, 990 w, 630 m, 580 w; nmr (CCl_4): τ 2.70 - 3.30 (multiplet, 8H, aromatic), 5.73 (doublet, 1H, H_1, $J_{1,7}$ = 3.0 Hz), 5.87 (triplet, 1H, H_4, $J_{4,\underline{trans}\text{-}8} \simeq J_{4,\underline{cis}\text{-}8}$ = 2.5 Hz), 8.32 (multiplet, 3H, $H_{\underline{trans}\text{-}8}$, $H_{\underline{cis}\text{-}8}$, H_7), 9.34 (singlet, 9H, tert-butyl); mass spectrum (115°, E.I.) m/e (relative intensity > 10%): 179 (16), 178 (100), weak but structurally significant peaks at 262 (M, 1.4) and 205 (1.2).

Anal. Calcd for $C_{20}H_{22}$: C, 91.54; H, 8.46. Found: C, 91.65; H, 8.45.

7-Carboxydibenzobicyclo[2.2.2.]octadiene, 21, - The procedure of Campaigne was modified (49). Silver nitrate (1.35 g, 0.0079 mole) was dissolved in water (3 ml) and the solution was then added to a solution of sodium hydroxide (0.63 g, 0.016 mole) in water (3 ml) with stirring. The brown suspension was cooled in ice and to it was added a solution of 7-formyldibenzobicyclo[2.2.2.]-octadiene, 4, (1.0 g, 0.0043 mole) in ether (5 ml) with

stirring. The mixture turned black with the formation of metallic silver. Stirring was continued for five minutes after the addition was complete, whereupon the mixture was filtered by vacuum filtration and the residue was washed copiously with ether. The ethereal solution was extracted twice with saturated sodium bicarbonate solution and the acid was recovered by addition of hydrochloric acid, followed by filtration. The acid was recrystallized from carbon tetrachloride and 0.86 g (0.0035 mole, 81%) of the white crystals was obtained, mp 186 - 186.5° (lit. 186 - 187° (50)); ir (CCl_4) cm^{-1}: 3510 w, 3000 s broad, 2960 s, 2710 m, 1700 s, 1515 m, 1465 s, 1455 s, 1415 s; nmr (CCl_4): τ -1.04 (singlet, 1H, COO<u>H</u>), 2.60 - 3.10 (multiplet, 8H, aromatic), 5.34 (doublet, 1H, H_1, $J_{1,7}$ = 2.25 Hz), 5.67 (triplet, 1H, H_4, $J_{4,\underline{cis}\text{-}8} \simeq J_{4,\underline{trans}\text{-}8}$ = 3.0 Hz), 7.13 (multiplet, 1H, H_7), 7.94 (multiplet, 2H, <u>cis</u>-H_8 and <u>trans</u>-H_8); mass spectrum (95°, E.I.) m/e (relative intensity > 10%: 250 (M, 17), 179 (18), 178 (100).

<u>Anal.</u> Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64. Found: C, 81.32; H, 5.57.

<u>Dibenzobicyclo[3.2.1.]octadiene, 7</u>,- A mixture of <u>exo</u>- and <u>endo</u>-4-chlorodibenzobicyclo[3.2.1.]octadiene (0.5 g, 0.0021 mole) was dissolved in ether (7 ml). Sodium (0.5 g, 0.0217 mole) was dissolved in liquid

ammonia (30 ml) cooled in an acetone/Dry Ice bath to -60°. The chloride solution was added slowly to the blue solution. After the addition was complete, the solution was kept cold for 5 minutes and the solution was then allowed to warm up to room temperature. The ethereal solution was then washed with water and dried over anhydrous sodium sulfate. After filtration of the drying agent, the solvent was removed by rotary evaporation to leave a pale yellow oil (0.28 g, 0.0014 mole, 66%). A portion of this oil (0.14 g) was dissolved in the minimum amount of 80:20/pentane:carbon tetrachloride and subjected to chromatography on acid-washed alumina (7 g) using the same solvent as eluent. The first two fractions of 75 ml yielded a total of 0.10 g of a waxy solid; mp: 35 - 36.5° (lit. 36 - 37° (27)). The nmr spectrum was identical to that reported for dibenzobicyclo[3.2.1.]-octadiene (28).

This compound was also formed as the hydrolysis product of the attempted reaction of formaldehyde with the Grignard reagent of 4-chlorodibenzobicyclo[3.2.1.]-octadiene.

Identification of Products for which Authentic Samples were not Available - 4-Methyldibenzobicyclo-[3.2.1.]octadiene, 13, - This minor product was collected by preparative glpc (see below); its stereochemistry

was not established; mp: 41 - 43.5°. Sufficient material was obtained for a mass spectral analysis: m/e (70°, E.I., relative intensity > 20%): 220 (M, 79), 219 (29), 206 (24), 205 (100), 204 (25), 178 (30).

Mass Measurement. Calcd for $C_{17}H_{16}$: 220.1252. Found: 220.1252.

exo-4-tert-Butyldibenzobicyclo[3.2.1.]octadiene, 12,

This product was collected by preparative glpc and analyzed by nmr, ir and mass spectrometry. Nmr ($CDCl_3$): τ 2.60 - 3.20 (multiplet, 8H, aromatic), 6.15 (doublet, 1H, H_1, $J_{1,anti\text{-}8}$ = 4.5 Hz), 6.32 (doublet, 1H, H_5, $J_{5,anti\text{-}8}$ = 4.8 Hz), 7.42 (doublet, 1H, $H_{endo\text{-}4}$, $J_{endo\text{-}4,5}$ = 1 Hz), 7.48 (doublet, 1H, $H_{syn\text{-}8}$, $J_{syn\text{-}8,anti\text{-}8}$ = 11.5 Hz), 7.78 (multiplet, 1H, $H_{anti\text{-}8}$), 8.80 (singlet, 9H, tert-butyl); ir (CCl_4) cm^{-1}: 3080 w, 3015 w, 2960 s, 2910 m, 2890 m, 1480 m, 1470 w, 1460 w, 1395 w, 1365 m, 1285 w, 1248 m, 1205 w, 910 w, 860 s, 694 w; mass spectrum (135°, E.I.) m/e (relative intensity > 10%): 262 (M, 14), 206 (37), 205 (100), 204 (11), 203 (12), 178 (11). Mp 77 - 77.5°. Anal. Calcd for $C_{20}H_{22}$: C, 91.54; H, 8.46. Found: C, 91.29; H, 8.26.

endo-4-tert-Butyldibenzobicyclo[3.2.1.]octadiene, 16,

The hydrocarbon was collected by glpc; mp: 73 - 75°. Nmr

($CDCl_3$): (incomplete) τ 2.65 - 3.15 (multiplet, aromatic), 8.90 (singlet, tert-butyl); mass spectrum (135°, E.I.) m/e (relative intensity > 10%): 262 (M, 10), 206 (42), 205 (100), 178 (20).

bis-4-(Dibenzobicyclo[3.2.1.]octadiene), 17,- The dimer was collected by preparative glpc. Three collection-reinjection-recollection cycles were required to free the compound from 7-formyldibenzobicyclo[2.2.2.]-octadiene, 4, which was the compound eluted soon after the dimer; mp: 41 - 43.5°. Mass spectrum: (150°, E.I.) m/e (relative intensity > 10%): 206 (22), 205 (100), 204 (12), 203 (13), 191 (14), 178 (11), weak but structurally significant peak at 410 (3.8).

Mass Measurement. Calcd for $C_{32}H_{26}$: 410.2036. Found: 410.2035.

III. PROCEDURE FOR REACTIONS

Reaction ampoules were made of thick-walled Pyrex tubes joined to 10/30 joints, the total volume of each tube being about 3 ml. The ampoules were cleaned with chromic acid, distilled water, concentrated ammonia and finally distilled water and were then oven-dried at 110°. In subdued light, a weighed amount of the aldehyde was measured into the ampoule, followed by an aliquot of a solution of the initiator in chlorobenzene (1 ml of a

solution containing tert-butylperpivalate (0.663 g, 0.0041 mole) in chlorobenzene (25 ml): i.e. 1 ml of a 1.52 M solution). The ampoules were then degassed by three cycles of freeze-thaw at ca. 10^{-5} mm. After degassing, the ampoules were sealed under vacuum, allowed to warm, shaken to ensure dissolution of the aldehyde, sheathed in wire cages and then placed in an oil-bath which was held to a constant temperature of 84° (125° in the case of the high-temperature reactions). The reactions were deemed complete after 8 hours ($t_{\frac{1}{2}}$ initiator = 45 minutes at 84° (38)). After this time, the ampoules were cooled to 77°K and opened. Immediately, an aliquot of a solution of biphenyl in chlorobenzene (1 ml of a 0.032 M solution) was added to the reaction ampoule. The thawed reaction mixture was then analyzed by glpc as described below.

In order to ascertain whether the products of the reactions were stable under the conditions of the reactions, authentic mixtures, where available, were heated with tert-butyl perpivalate in chlorobenzene and were analyzed in the same way as were the reaction mixtures. The products so tested were stable to the reaction and analysis conditions. Also tested in this way were 7-tert-butyldibenzobicyclo[2.2.2.]octadiene and 7-tert-butoxydibenzobicyclo[2.2.2.]octadiene; even though these compounds were not found as products, they were considered possible products and the control was undertaken to

ensure that they had not been transformed into a true reaction product. Both compounds were stable to the conditions of reaction and analysis and therefore were not reaction products. 7-Formyldibenzobicyclo[2.2.2.]octadiene was found to decompose under the conditions of analysis, but the keeping of the column temperature at or below 150° minimized the problem. If an all-glass system were not used, the extent of the retro-Diels Alder reaction became excessive. Anthracene, the product of this decomposition, appeared on the glpc trace as an uneven and drawn-out peak. Two collections were made of this peak: the first of the first half of the peak and the second of the second half. Upon reinjection, both the collections gave one peak of the same retention time as anthracene, thus confirming that the decomposition was taking place on the column and that only one compound was represented by the original peak.

IV. ANALYSIS OF REACTANTS AND PRODUCTS

Gas-Liquid Partition Chromatography (glpc) - One instrument, a Hewlett-Packard H.P. Model 402, was used throughout. It was fitted with a splitting device in the column outlet which enabled collections to be made under the same conditions as were employed in the analyses. The system was of the all-glass type with on-column injection. Detection was by means of a flame-ionization

detector. The carrier gas was helium, maintained at a constant flow rate of 100 ml/minute. Three all-glass columns were used:

a) 4 ft by 0.25 in NeoPentyl Glycol Succinate (NPGS), 10%, Chromosorb P, A/W, 60/80 mesh

b) 2 ft by 0.25 in NPGS, 10%, Chromosorb P, A/W, 60/80 mesh

c) 8 ft by 0.25 in SE-30, 5% Chromosorb W, A/W, 60/80 mesh.

The first of these columns was capable of separating biphenyl, dibenzobicyclo[2.2.2.]octadiene,11, dibenzobicyclo[3.2.1.]octadiene,7, 7-methyldibenzobicyclo-[2.2.2.]octadiene,19, 4-methyldibenzobicyclo[3.2.1.]-octadiene,13, anthracene, 7-tert-butyldibenzobicyclo-[2.2.2.]octadiene,20, and exo-4-tert-butyldibenzobicyclo-[3.2.1.]octadiene,12, though not all of these compounds were found in the reaction mixtures. The second column could separate biphenyl, exo-4-tert-butyldibenzobicyclo-[3.2.1.]octadiene,12, endo-4-tert-butyldibenzobicyclo-[3.2.1.]octadiene,16, 7-tert-butoxydibenzobicyclo[2.2.2.]-octadiene, 18, exo-2-tert-butoxydibenzobicyclo[3.2.1.]-octadiene,14, endo-2-tert-butoxydibenzobicyclo[3.2.1.]-octadiene,15, bis-4-(dibenzobicyclo[3.2.1.]octadiene), 17, 7-formyldibenzobicyclo[2.2.2.]octadiene,4,and 7-carboxydibenzobicyclo[2.2.2.]octadiene,28, though not

all of these compounds were found in the reaction mixtures. This column was also able to separate dibenzobicyclo[3.2.1.]octadien-2-one from 2-formyldibenzobicyclo-[3.2.1.]octadiene.

Analyses were carried out in triplicate. Peak areas were measured either by multiplying peak height by peak width at one-half peak height, or by a planimeter if the peak did not resemble a Gaussian curve. The area ratio of the product to added biphenyl as a standard was used to calculate the concentration of the product present by multiplying the area ratio with known amount of biphenyl. The area ratio was corrected by a calibration factor which was obtained by comparing the area ratio with the mole ratio of accurately prepared solutions of the two hydrocarbons 7 and 11 and the aldehyde 4 and biphenyl in chlorobenzene. Retention time comparison and peak enhancement were obtained by the addition of authentic material to a portion of the sample and re-analysis by glpc. At least two columns were used in the comparisons of the retention times.

Spectral Measurements. Infrared (ir) spectra were recorded on a Perkin-Elmer Model 421 Recording Infrared Spectrophotometer. Nuclear magnetic resonance (nmr) proton spectra were obtained on a Varian Associates A-60 instrument, or, where sample size dictated, on a Varian

Associates HR-100 instrument fitted with Fourier Transform capability. Chemical shifts are expressed in τ units and are relative to tetramethylsilane (TMS, τ = 10.00). Mass spectra were obtained on an A.E.I. Model M.S. 12. Mass measurement was performed on an A.E.I. Model M.S. 9.

Microanaylses. Microanalyses were performed in the microanalytical laboratory, Chemistry Department, University of Alberta, Edmonton.

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